

Supporting Information for

Highly diastereoselective annulation of 2-substituted 3-nitro-2H-chromenes with hemicurcuminoids and curcuminoids *via* a double and triple Michael reaction cascade

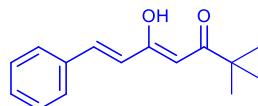
Nikolay S. Zimnitskiy, Alexey Yu. Barkov, Ivan A. Kochnev, Igor B. Kutyashev,
Vladislav Yu. Korotaev*, Vyacheslav Ya. Sosnovskikh

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General procedures

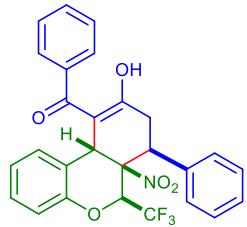
IR spectra were recorded on a Shimadzu IRSpirit-T spectrometer equipped with an ATR accessory. NMR spectra were recorded on Bruker Avance III-500 (^1H , 500 MHz; ^{19}F , 376 MHz; ^{13}C , 126 MHz) and Bruker Avance NEO (^1H , 600 MHz; ^{13}C , 151 MHz) spectrometers in CDCl_3 . The chemical shifts (δ) are reported in ppm relative to the internal standard TMS (^1H , ^{19}F NMR) or residual signal of the solvent (^{13}C NMR, 77.16 ppm). 2D ^1H - ^1H NOESY spectra were acquired on a Bruker AVANCE NEO (600 MHz) spectrometer with 0.3 s mixing time. The HRMS spectra were obtained using the UHR-QqTOF maXis Impact HD (Bruker Daltonics) mass spectrometer. Elemental analysis was performed on a PerkinElmer PE 2400 automatic analyser. Melting points were determined on an SMP40 apparatus. All solvents used were dried and distilled by standard procedures. The starting chromenes **1a-g**,^{1a} **1k-m**,^{1b} **2a-c**,^{1c} enediones **3a-p**^{2a}, **3q**^{2b} and curcuminoids **4a,b**^{2c} were prepared according to described procedures. Curcumin **4c** was purchased from Sigma-Aldrich and used as is.



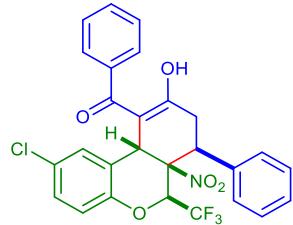
(4Z,6E)-5-Hydroxy-2,2-dimethyl-7-phenylhepta-4,6-dien-3-one (**3r**). 5,5-Dimethylhexane-2,4-dione (1 g, 7 mmol) has been added to a mixture of B_2O_3 (0.34 g, 4.9 mmol) in EtOAc (5 mL) and $\text{B}(\text{OMe})_3$ (5 mL) and stirred at 60 °C for 30 min. After that the reaction was cooled down and a benzaldehyde (0.75 g, 7 mmol) was added to it, followed by dropwise addition of a 20% solution of BnNH_2 (0.5 mL) in EtOAc within 1 h. The reaction was stirred overnight, then acidified with 1M HCl (4 ml) and stirred at 50 °C for 1 h. The resulting mixture was diluted with H_2O (20 mL) and the precipitate was collected by filtration. Yellowish precipitate was washed with water (100 mL), dried under reduced pressure and recrystallized from MeOH (7 mL) to give the target enedione. Yield 903 mg (56%), light yellow powder, mp 102–103 °C (lit.³ 101 °C). IR (ATR): 2977, 1639, 1585, 1564, 1471, 1423 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.21 (s, 9H), 5.80 (s, 1H), 6.53 (d, J = 15.9 Hz, 1H), 7.32–7.41 (m, 3H), 7.53 (dd, J = 7.7, 1.6 Hz, 2H), 7.59 (d, J = 15.9 Hz, 1H), 15.67 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 27.3 (3C), 40.9, 97.0, 123.5, 128.1 (2C), 129.0 (2C), 129.9, 135.3, 139.4, 178.1, 207.0. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 78.22; H, 7.88.

General procedure for the synthesis of 10-arylohexahydro-9*H*-benzo[*c*]chromen-9-ones 5. A mixture of the appropriate 2*H*-nitrochromene **1** (0.25 mmol), enedione **3** (0.25 mmol) and K_2CO_3 (9 mg, 0.06 mmol) was dissolved in dichloromethane (2 mL) and stirred for 48 h at room temperature (TLC control, CH_2Cl_2 -hexane (1:1)). Upon completion of the reaction, formed orange solution was quenched with hexane (5 ml), precipitate was filtered off and the residue was evaporated under reduced pressure

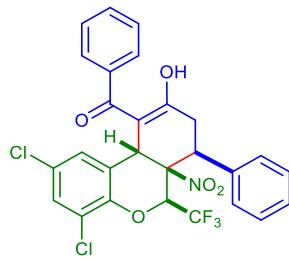
to complete dryness. Residue was washed with cold methanol to give target products **5**.



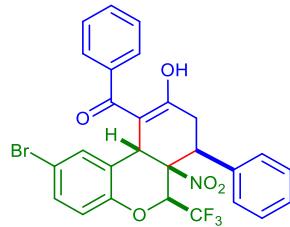
((6S,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5aa).* Obtained from **1a** (61 mg) and **3a** (63 mg) according to the general procedure. Yield 122 mg (98%), white powder, mp 210–211 °C. IR (ATR): 1600, 1583, 1553, 1486, 1454, 1374, 1270 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.72 (dd, *J* = 19.1, 5.4 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.74 (dd, *J* = 13.4, 5.4 Hz, 1H), 4.93 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.20 (s, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.04–7.11 (m, 2H), 7.22–7.33 (m, 3H), 7.39–7.52 (m, 6H), 7.79–7.87 (m, 2H), 16.32 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.19 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.3 (q, ³J_{C,F} = 1.6 Hz, C-6a), 36.7, 41.5, 74.0 (q, ²J_{C,F} = 31.1 Hz, C-6), 85.5, 106.8, 116.9, 122.9, 123.1, 123.3 (q, ¹J_{C,F} = 287.6 Hz, CF₃), 127.8 (2C), 128.8 (2C), 128.9 (2C), 129.2, 129.3, 129.6, 129.7 (2C), 131.4, 134.1, 136.1, 149.0, 187.1, 190.3. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₁F₃NO₅ 496.1366, found 496.1359.



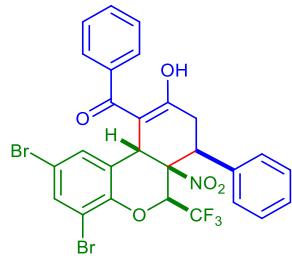
((6S,6aR*,7S*,10aR*)-2-Chloro-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ba).* Obtained from **1b** (70 mg) and **3a** (63 mg) according to the general procedure. Yield 122 mg (92%), white powder, mp 180–181 °C. IR (ATR): 1600, 1557, 1481, 1454, 1379, 1274 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.75 (dd, *J* = 19.1, 5.5 Hz, 1H), 3.06 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.68 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.92 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.18 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 7.05 (s, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.23–7.26 (m, 2H), 7.39–7.46 (m, 3H), 7.46–7.53 (m, 3H), 7.78–7.84 (m, 2H), 16.37 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.20 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.6 (q, ³J_{C,F} = 1.5 Hz, C-6a), 41.6, 74.0 (q, ²J_{C,F} 31.0 Hz, C-6), 85.2, 106.3, 118.3, 123.2 (q, ¹J_{C,F} 287.6 Hz, CF₃), 124.6, 127.7 (2C), 128.4, 128.9 (2C), 129.1 (3C), 129.4, 129.6, 129.7 (2C), 131.5, 133.8, 135.9, 147.6, 187.2, 190.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₀ClF₃NO₅ 530.0977, found 530.0994.



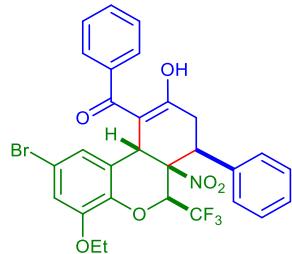
((6S*,6aR*,7S*,10aR*)-2,4-Dichloro-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ca). Obtained from **1c** (79 mg) and **3a** (63 mg) according to the general procedure. Yield 136 mg (96%), white powder, mp 178–179 °C. IR (ATR): 1603, 1554, 1491, 1449, 1378, 1276 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.77 (dd, *J* = 19.1, 5.5 Hz, 1H), 3.07 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.62 (dd, *J* = 13.4, 5.5 Hz, 1H), 5.04 (q, ³J_{H,F} = 6.9 Hz, 1H), 5.20 (s, 1H), 6.96 (d, *J* = 1.4 Hz, 1H), 7.21–7.26 (m, 2H), 7.33 (d, *J* = 1.4 Hz, 1H), 7.41–7.47 (m, 3H), 7.47–7.54 (m, 3H), 7.76–7.82 (m, 2H), 16.36 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.17 (d, *J* = 6.9 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.9 (q, ³J_{C,F} = 1.6 Hz, C-6a), 41.8, 74.3 (q, ²J_{C,F} = 31.4 Hz, C-6), 85.0, 106.0, 123.0 (q, ¹J_{C,F} = 287.6 Hz, CF₃), 123.3, 125.9, 127.6 (3C), 128.2, 129.1 (2C), 129.2 (2C), 129.6, 129.7 (2C), 129.9, 131.6, 133.5, 135.8, 143.8, 187.2, 190.7. Anal. Calcd for C₂₇H₁₈Cl₂F₃NO₅·H₂O: C, 55.69; H, 3.46; N, 2.41. Found: C, 55.41; H, 3.14; N, 2.40.



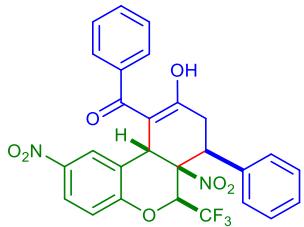
((6S*,6aR*,7S*,10aR*)-2-Bromo-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5da). Obtained from **1d** (81 mg) and **3a** (63 mg) according to the general procedure. Yield 131 mg (91%), white powder, mp 173–174 °C. IR (ATR): 1600, 1577, 1556, 1478, 1421, 1378, 1274 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.76 (dd, *J* = 19.1, 5.5 Hz, 1H), 3.06 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.67 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.91 (q, ³J_{H,F} = 6.9 Hz, 1H), 5.18 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.23–7.27 (m, 2H), 7.34 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.41–7.45 (m, 3H), 7.48–7.52 (m, 3H), 7.78–7.83 (m, 2H), 16.38 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.18 (d, *J* = 6.9 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.7 (q, ³J_{C,F} = 2.3 Hz, C-6a), 41.6, 74.0 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.1, 106.2, 115.6, 118.7, 123.1 (q, ¹J_{C,F} = 287.6 Hz, CF₃), 125.0, 127.6 (2C), 128.9 (2C), 129.1 (2C), 129.4, 129.7 (2C), 131.5, 132.0, 132.5, 133.8, 135.9, 148.2, 187.1, 190.8. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₀BrF₃NO₅ 574.0471, found 574.0464.



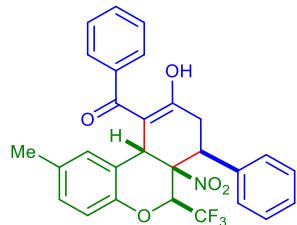
((6S,6aR*,7S*,10aR*)-2,4-Dibromo-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ea).* Obtained from **1e** (101 mg) and **3a** (63 mg) according to the general procedure. Yield 131 mg (80%), white powder, mp 219–220 °C. IR (ATR): 1604, 1553, 1492, 1442, 1376, 1273 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.77 (dd, *J* = 19.1, 5.5 Hz, 1H), 3.07 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.61 (dd, *J* = 13.4, 5.5 Hz, 1H), 5.03 (q, ³J_{H,F} = 6.9 Hz, 1H), 5.22 (s, 1H), 7.14 (d, *J* = 1.5 Hz, 1H), 7.22–7.27 (m, 2H), 7.42–7.47 (m, 3H), 7.47–7.53 (m, 3H), 7.62 (d, *J* = 1.5 Hz, 1H), 7.74–7.83 (m, 2H), 16.37 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.13 (d, *J* = 6.9 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.8 (q, ³J_{C,F} = 1.3 Hz, C-6a), 41.7, 74.4 (q, ²J_{C,F} = 31.5 Hz, C-6), 84.9, 106.0, 112.0, 115.5, 122.9 (q, ¹J_{C,F} = 287.5 Hz, CF₃), 126.1, 127.6 (2C), 129.1 (2C), 129.2 (2C), 129.6, 129.7 (2C), 131.3, 131.6, 133.4, 135.5, 135.8, 145.2, 187.1, 190.9. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₁₉Br₂F₃NO₅ 651.9577, found 651.9568.



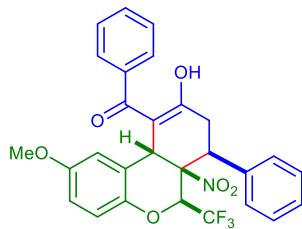
((6S,6aR*,7S*,10aR*)-2-Bromo-4-ethoxy-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5fa).* Obtained from **1f** (92 mg) and **3a** (63 mg) according to the general procedure. Yield 138 mg (89%), white powder, mp 226–227 °C. IR (ATR): 1603, 1573, 1549, 1468, 1454, 1374, 1264 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.45 (t, *J* = 7.0 Hz, 3H), 2.75 (dd, *J* = 19.1, 5.6 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.2 Hz, 1H), 3.71 (dd, *J* = 13.2, 5.6 Hz, 1H), 4.10 (dq, *J* = 9.7, 7.0 Hz, 1H), 4.11 (dq, *J* = 9.7, 7.0 Hz, 1H), 5.01 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.16 (s, 1H), 6.78 (s, 1H), 6.94 (s, 1H), 7.23–7.29 (m, 2H), 7.40–7.45 (m, 3H), 7.46–7.52 (m, 3H), 7.77–7.82 (m, 2H), 16.34 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.36 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 14.8, 35.3, 36.7 (q, ³J_{C,F} = 1.3 Hz, C-6a), 41.7, 65.7, 74.0 (q, ²J_{C,F} = 31.1 Hz, C-6), 85.3, 106.4, 115.0, 116.8, 123.1, 123.2 (q, ¹J_{C,F} = 287.9 Hz, CF₃), 125.4, 128.97 (2C), 129.0 (2C), 129.0 (2C), 129.3, 129.7 (2C), 131.4, 134.0, 136.0, 138.4, 148.7, 187.2, 190.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₉H₂₄BrF₃NO₆ 618.0734, found 618.0722.



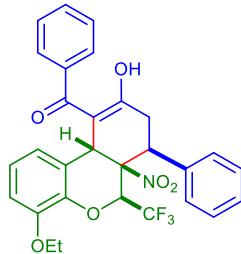
((6S,6aR*,7S*,10aR*)-9-Hydroxy-2,6a-dinitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ga).* Obtained from **1g** (73 mg) and **3a** (63 mg) according to the general procedure. Yield 116 mg (82%), white powder, mp 222–223 °C. IR (ATR): 1605, 1585, 1557, 1530, 1476, 1382, 1344, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.78 (dd, *J* = 19.1, 5.2 Hz, 1H), 3.09 (dd, *J* = 19.1, 13.5 Hz, 1H), 3.58 (dd, *J* = 13.5, 5.2 Hz, 1H), 5.03 (q, ³J_{H,F} = 6.8 Hz, 1H), 5.28 (s, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 7.22–7.25 (m, 2H), 7.43–7.52 (m, 6H), 7.86–7.91 (m, 2H), 8.08 (d, *J* = 2.4 Hz, 1H), 8.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 16.45 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.25 (d, *J* = 6.8 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.1, 36.6 (q, ³J_{C,F} = 1.5 Hz, C-6a), 41.7, 74.4 (q, ²J_{C,F} = 31.5 Hz, C-6), 84.7, 105.7, 117.8, 122.9 (q, ¹J_{C,F} = 287.3 Hz, CF₃), 124.1, 125.3, 125.7, 127.6 (2C), 129.1 (2C), 129.2 (2C), 129.6 (2C), 129.7, 131.6, 133.3, 135.8, 143.5, 153.8, 186.9, 191.4. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₀F₃N₂O₇ 541.1217, found 541.1211.



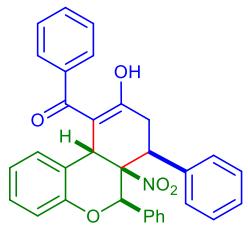
((6S,6aR*,7S*,10aR*)-9-Hydroxy-2-methyl-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ha).* Obtained from **1h** (65 mg) and **3a** (63 mg) according to the general procedure. Yield 116 mg (81%), white powder, mp 186–187 °C. IR (ATR): 1601, 1591, 1557, 1549, 1494, 1374, 1342, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.26 (s, 3H), 2.72 (dd, *J* = 19.1, 5.6 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.75 (dd, *J* = 13.4, 5.6 Hz, 1H), 4.89 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.16 (s, 1H), 6.86 (s, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.26–7.30 (m, 2H), 7.39–7.44 (m, 3H), 7.44–7.50 (m, 3H), 7.79–7.85 (m, 2H), 16.33 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.20 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 20.9, 35.3, 36.6 (q, ³J_{C,F} = 1.3 Hz, C-6a), 41.5, 73.9 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.7, 106.9, 116.7, 122.4, 123.4 (q, ¹J_{C,F} = 287.9 Hz, CF₃), 127.8 (2C), 128.8 (2C), 128.9 (2C), 129.3, 129.6, 129.7 (2C), 130.1, 131.3, 132.5, 134.2, 136.3, 146.8, 187.0, 190.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₃F₃NO₅ 510.1523, found 510.1516.



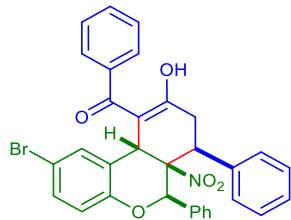
((6S,6aR*,7S*,10aR*)-9-Hydroxy-2-methoxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ia).* Obtained from **1i** (69 mg) and **3a** (63 mg) according to the general procedure. Yield 122 mg (92%), white powder, mp 146–147 °C. IR (ATR): 1603, 1553, 1492, 1467, 1373, 1357, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.73 (dd, *J* = 19.1, 5.6 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.73 (s, 3H), 3.77 (dd, *J* = 13.4, 5.6 Hz, 1H), 4.88 (q, ³J_{H,F} = 7.2 Hz, 1H), 5.22 (s, 1H), 6.56 (d, *J* = 2.7 Hz, 1H), 6.78 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 7.26–7.31 (m, 2H), 7.39–7.44 (m, 3H), 7.45–7.52 (m, 3H), 7.82–7.88 (m, 2H), 16.37 (s, 1H); ¹⁹F NMR (471 MHz, CDCl₃) δ 91.27 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.4, 36.9 (br. s, C-6a), 41.6, 55.9, 74.0 (q, ²J_{C,F} = 30.9 Hz, C-6), 85.8, 106.9, 113.9, 115.4, 117.6, 123.4 (q, ¹J_{C,F} = 288.1 Hz, CF₃), 123.6, 127.8 (2C), 128.8 (2C), 129.0 (2C), 129.3, 129.8 (2C), 131.5, 134.3, 136.2, 142.7, 155.2, 187.3, 190.3. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₃F₃NO₆ 526.1472, found 526.1474.



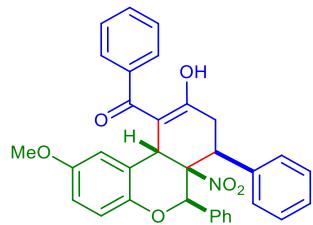
((6S,6aR*,7S*,10aR*)-4-Ethoxy-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ja).* Obtained from **1j** (72 mg) and **3a** (63 mg) according to the general procedure. Yield 121 mg (90%), white powder, mp 195–196 °C. IR (ATR): 1602, 1585, 1553, 1472, 1377, 1324, 1273 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.44 (t, *J* = 6.9 Hz, 3H), 2.72 (dd, *J* = 19.0, 5.5 Hz, 1H), 3.04 (dd, *J* = 19.0, 13.1 Hz, 1H), 3.78 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.13 (q, *J* = 6.9 Hz, 2H), 5.04 (q, *J* = 6.9 Hz, 1H), 5.19 (s, 1H), 6.67 (d, ³J_{H,F} = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 7.23–7.32 (m, 2H), 7.37–7.52 (m, 6H), 7.78–7.86 (m, 2H), 16.28 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.43 (d, *J* = 6.9 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 14.9, 35.4, 36.8 (br. s, C-6a), 41.6, 65.3, 73.9 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.5, 107.0, 113.7, 120.5, 122.6, 123.3 (q, ¹J_{C,F} = 287.8 Hz, CF₃), 124.0, 127.9 (2C), 128.88 (2C), 128.9 (2C), 129.2, 129.7 (2C), 131.3, 134.3, 136.1, 139.2, 147.9, 187.2, 190.1. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₉H₂₅F₃NO₆ 540.1628, found 540.1627.



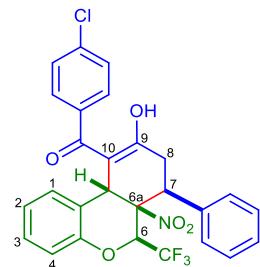
((6S,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ka).* Obtained from **1k** (64 mg) and **3a** (63 mg) according to the general procedure. Yield 113 mg (90%), white powder, mp 198–199 °C. IR (ATR): 1616, 1603, 1581, 1544, 1483, 1451, 1399, 1278, 1224 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.74 (dd, *J* = 19.0, 5.1 Hz, 1H), 3.11 (dd, *J* = 19.0, 13.6 Hz, 1H), 3.74 (dd, *J* = 13.6, 5.1 Hz, 1H), 5.07 (s, 1H), 5.45 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 7.03–7.09 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.23–7.33 (m, 4H), 7.37–7.47 (m, 6H), 7.64 (d, *J* = 7.4 Hz, 2H), 16.44 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.58, 35.64, 41.4, 78.2, 91.2, 106.6, 116.6, 121.7, 123.3, 126.9 (2C), 127.8 (2C), 128.5 (2C), 128.6 (3C), 128.7 (2C), 129.1, 129.4, 129.5, 130.2 (2C), 131.0, 135.4, 135.9, 136.4, 151.1, 187.4, 191.5. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₂H₂₆NO₅ 504.1805, found 504.1807.



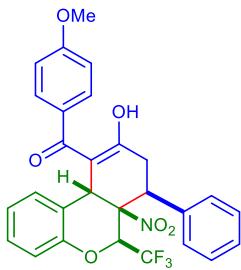
((6R,6aR*,7S*,10aR*)-2-Bromo-9-hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5la).* Obtained from **1l** (83 mg) and **3a** (63 mg) according to the general procedure. Yield 117 mg (80%), white powder, mp 197–198 °C. IR (ATR): 1622, 1596, 1544, 1472, 1454, 1398, 1263, 1227 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.78 (dd, *J* = 19.2, 5.4 Hz, 1H), 3.12 (dd, *J* = 19.2, 13.5 Hz, 1H), 3.67 (dd, *J* = 13.5, 5.4 Hz, 1H), 5.06 (s, 1H), 5.43 (s, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 1H), 7.13–7.18 (m, 3H), 7.28–7.37 (m, 4H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.41–7.47 (m, 4H), 7.61 (d, *J* = 7.5 Hz, 2H), 16.48 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.5 (2C), 41.5, 78.3, 90.7, 106.0, 114.1, 118.4, 125.4, 126.8 (2C), 127.6 (2C), 128.5 (2C), 128.7 (3C), 128.8 (2C), 129.6, 130.2 (2C), 131.2, 131.9, 132.4, 135.1, 135.4, 136.2, 150.2, 187.4, 191.9. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₂H₂₄BrNNaO₅ 604.0730, found 604.0727.



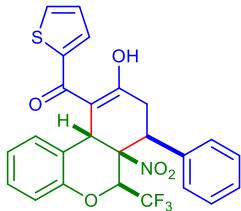
((6R,6aR*,7S*,10aR*)-9-Hydroxy-2-methoxy-6a-nitro-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ma).* Obtained from **1m** (71 mg) and **3a** (63 mg) according to the general procedure. Yield 105 mg (79%), white powder, mp 185–186 °C. IR (ATR): 1600, 1577, 1541, 1489, 1429, 1403, 1264, 1237 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.75 (dd, *J* = 19.1, 5.4 Hz, 1H), 3.12 (dd, *J* = 19.1, 13.6 Hz, 1H), 3.75 (s, 3H), 3.77 (dd, *J* = 13.6, 5.4 Hz, 1H), 5.09 (s, 1H), 5.40 (s, 1H), 6.56 (s, 1H), 6.80–6.87 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.25–7.34 (m, 3H), 7.38–7.48 (m, 6H), 7.65 (d, *J* = 7.5 Hz, 2H), 16.50 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 35.9, 41.5, 55.8, 78.1, 91.4, 106.6, 113.7, 115.5, 117.3, 124.0, 126.9 (2C), 127.8 (2C), 128.4 (2C), 128.6, 128.62 (2C), 128.7 (2C), 129.4, 130.3 (2C), 131.2, 135.4, 136.0, 136.4, 144.8, 154.3, 187.7, 191.4. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₃H₂₈NO₆ 534.1911, found 534.1907.



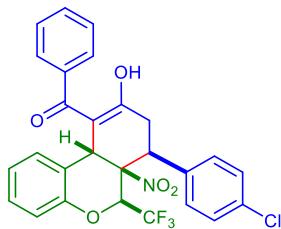
(4-Chlorophenyl)((6S,6aR*,7S*,10aR*)-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5ab).* Obtained from **1a** (61 mg) and **3b** (71 mg) according to the general procedure. Yield 130 mg (98%), white powder, mp 163–164 °C. IR (ATR): 1634, 1585, 1549, 1484, 1454, 1374, 1273 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.73 (dd, *J* = 19.1, 5.6 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.74 (dd, *J* = 13.4, 5.6 Hz, 1H), 4.93 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.12 (s, 1H), 7.01–7.03 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.26–7.30 (m, 3H), 7.40–7.47 (m, 5H), 7.76–7.81 (m, 2H), 16.22 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.18 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.3, 36.8 (q, ³J_{C,F} = 1.2 Hz, C-6a), 41.5, 74.0 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.5, 106.8, 117.1, 122.7, 123.2, 123.3 (q, ¹J_{C,F} = 287.8 Hz, CF₃), 128.9 (2C), 129.0 (2C), 129.3 (2C), 129.3 (2C), 129.4, 129.7, 129.7, 134.0, 134.5, 137.8, 149.1, 187.3, 189.0. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₀ClF₃NO₅ 530.0977, found 530.0976.



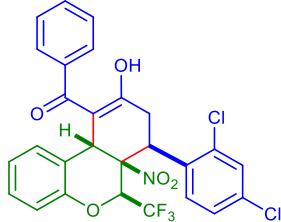
((6S,6aR*,7S*,10aR*)-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5ac).* Obtained from **1a** (61 mg) and **3c** (70 mg) according to the general procedure. Yield 123 mg (94%), white powder, mp 154–155 °C. IR (ATR): 1597, 1584, 1547, 1484, 1454, 1374, 1272 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.0, 5.6 Hz, 1H), 3.04 (dd, *J* = 19.0, 13.4 Hz, 1H), 3.74 (dd, *J* = 13.4, 5.6 Hz, 1H), 3.83 (s, 3H), 4.94 (q, ³*J*_{H,F} = 7.1 Hz, 1H), 5.27 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.23–7.30 (m, 3H), 7.40–7.44 (m, 3H), 7.83 (d, *J* = 8.8 Hz, 2H), 16.43 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.20 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.1, 36.8 (q, ³*J*_{C,F} = 1.4 Hz, C-6a), 41.4, 55.5, 74.0 (q, ²*J*_{C,F} = 31.1 Hz, C-6), 85.6, 106.6, 114.3 (2C), 116.9, 123.1, 123.1, 123.4 (q, ¹*J*_{C,F} = 287.9 Hz, CF₃), 128.8 (2C), 129.2, 129.3, 129.5, 129.7, 129.7 (2C), 130.0 (2C), 134.2, 149.0, 162.2, 186.1, 190.2. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₃F₃NO₆ 526.1472, found 526.1468.



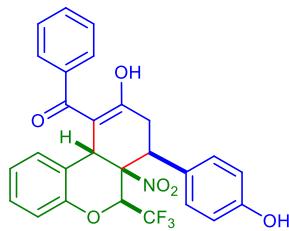
((6S,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(thiophen-2-yl)methanone (5ad).* Obtained from **1a** (61 mg) and **3d** (64 mg) according to the general procedure. Yield 119 mg (95%), white powder, mp 168–169 °C. IR (ATR): 1697, 1582, 1547, 1484, 1454, 1374, 1278 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.74 (dd, *J* = 19.2, 5.7 Hz, 1H), 3.03 (dd, *J* = 19.2, 13.4 Hz, 1H), 3.78 (dd, *J* = 13.4, 5.7 Hz, 1H), 4.96 (q, ³*J*_{H,F} = 7.1 Hz, 1H), 5.41 (s, 1H), 7.01–7.06 (m, 1H), 7.12 (dd, *J* = 4.8, 4.1 Hz, 1H), 7.17 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 5.6, 3.7 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.40–7.45 (m, 3H), 7.67–7.71 (m, 2H), 17.15 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 90.94 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.3, 37.4 (q, ³*J*_{C,F} = 1.6 Hz, C-6a), 41.3, 73.9 (q, ²*J*_{C,F} = 31.0 Hz, C-6), 85.5, 105.7, 117.1, 121.9, 123.1, 123.5 (q, ¹*J*_{C,F} = 286.3 Hz, CF₃), 128.7, 128.8 (2C), 129.3, 129.8 (2C), 129.9, 130.3, 132.2, 133.4, 134.1, 139.6, 149.6, 181.2, 187.4. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₅H₁₉F₃NO₅S 502.0931, found 502.0924.



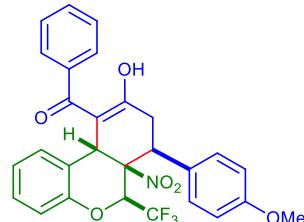
((6S,6aR*,7S*,10aR*)-7-(4-Chlorophenyl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ae).* Obtained from **1a** (61 mg) and **3e** (71 mg) according to the general procedure. Yield 125 mg (94%), white powder, mp 162–163 °C. IR (ATR): 1645, 1586, 1549, 1485, 1456, 1374, 1277 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.0, 5.5 Hz, 1H), 2.99 (dd, *J* = 19.0, 13.4 Hz, 1H), 3.72 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.88 (q, ³*J*_{H,F} = 7.0 Hz, 1H), 5.21 (s, 1H), 7.02 (dd, *J* = 11.0, 4.1 Hz, 1H), 7.07 (t, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.23–7.27 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.44–7.51 (m, 3H), 7.83 (dd, *J* = 7.5, 2.0 Hz, 2H), 16.31 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.01 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.7 (d, ³*J*_{C,F} = 1.1 Hz, C-6a), 41.0, 74.0 (q, ²*J*_{C,F} = 31.2 Hz, C-6), 85.5, 106.7, 116.9, 122.9, 123.2, 123.2 (q, ¹*J*_{C,F} = 287.8 Hz, CF₃), 127.8 (2C), 129.0 (2C), 129.1 (2C), 129.2, 129.7, 131.1 (2C), 131.5, 132.7, 135.4, 136.1, 148.9, 186.5, 190.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₀ClF₃NO₅ 530.0977, found 530.0985.



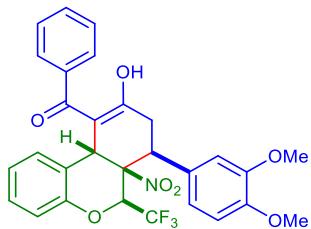
((6S,6aR*,7S*,10aR*)-7-(2,4-Dichlorophenyl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5af).* Obtained from **1a** (61 mg) and **3f** (80 mg) according to the general procedure. Yield 132 mg (94%), white powder, mp 162–163 °C. IR (ATR): 1645, 1586, 1549, 1485, 1456, 1374, 1277 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.61 (dd, *J* = 18.2, 7.4 Hz, 1H), 2.67 (dd, *J* = 18.2, 8.8 Hz, 1H), 4.54 (dd, *J* = 8.8, 7.4 Hz, 1H), 5.11 (s, 1H), 5.15 (q, ³*J*_{H,F} = 6.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.23–7.31 (m, 2H), 7.42–7.52 (m, 4H), 7.75–7.80 (m, 2H), 16.35 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 92.20 (d, *J* = 6.5 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 37.5 (q, ³*J*_{C,F} = 1.7 Hz, C-6a), 38.1, 38.2, 75.0 (q, ²*J*_{C,F} = 30.8 Hz, C-6), 86.6, 107.2, 117.4, 122.0, 123.2 (q, ¹*J*_{C,F} = 290.0 Hz, CF₃), 123.3, 127.7 (2C), 128.0, 128.6, 129.0 (2C), 129.6, 130.0, 130.3, 131.6, 132.9, 135.3, 135.6, 136.3, 149.9, 188.1, 189.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₁₉Cl₂F₃NO₅ 564.0587, found 564.0582.



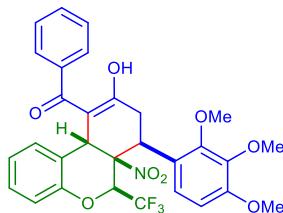
((6S,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-hydroxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ag).* Obtained from **1a** (61 mg) and **3g** (67 mg) according to the general procedure. Yield 99 mg (77%), yellow powder, mp 159–160 °C. IR (ATR): 3330, 1600, 1585, 1549, 1484, 1454, 1371, 1268 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.69 (dd, *J* = 19.1, 5.5 Hz, 1H), 2.98 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.68 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.92 (s, 1H), 4.93 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.18 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.03–7.09 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.44–7.49 (m, 3H), 7.80–7.84 (m, 2H), 16.31 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.15 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 36.7 (q, ³J_{C,F} = 1.3 Hz, C-6a), 40.9, 74.0 (q, ²J_{C,F} = 30.9 Hz, C-6), 85.6, 106.9, 115.7 (2C), 116.9, 123.0, 123.1, 123.4 (q, ¹J_{C,F} = 287.7 Hz, CF₃), 126.2, 127.8 (2C), 128.9 (2C), 129.2, 129.5, 131.0 (2C), 131.4, 136.1, 149.1, 156.3, 187.2, 190.3. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₂₇H₂₀F₃NNaO₆ 534.1135, found 534.1132.



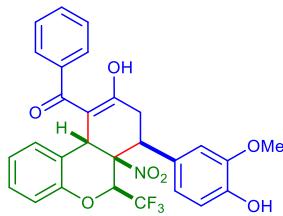
((6S,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ah).* Obtained from **1a** (61 mg) and **3h** (70 mg) according to the general procedure. Yield 129 mg (98%), white powder, mp 181–182 °C. IR (ATR): 1610, 1601, 1585, 1547, 1487, 1454, 1373, 1258 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.1, 5.5 Hz, 1H), 2.99 (dd, *J* = 19.1, 13.4 Hz, 1H), 3.70 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.85 (s, 3H), 4.94 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.19 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 15.0, 8.0 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.43–7.50 (m, 3H), 7.81–7.84 (m, 2H), 16.32 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.16 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.5, 36.6 (br. s, C-6a), 40.8, 55.4, 74.0 (q, ²J_{C,F} = 31.1 Hz, C-6), 85.6, 106.9, 114.2 (2C), 116.9, 123.0, 123.1, 123.4 (q, ¹J_{C,F} = 287.5 Hz, CF₃), 125.9, 127.8 (2C), 128.9 (2C), 129.2, 129.5, 130.8 (2C), 131.4, 136.1, 149.1, 160.2, 187.2, 190.3. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₃F₃NO₆ 526.1472, found 526.1467.



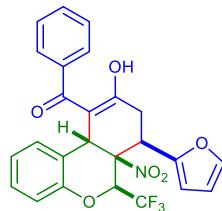
*((6*S**,6*a**R**,7*S**,10*a**R**)-7-(3,4-Methoxyphenyl)-9-hydroxy-6*a*-nitro-6-(trifluoromethyl)-6*a*,7,8,10*a*-tetrahydro-6*H*-benzo[*c*]chromen-10-yl)(phenyl)methanone (**5ai**).* Obtained from **1a** (61 mg) and **3i** (78 mg) according to the general procedure. Yield 126 mg (90%), light-yellow powder, mp 183–184 °C. IR (ATR): 1607, 1595, 1583, 1552, 1485, 1453, 1373, 1249 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 2.72 (dd, *J* = 19.0, 5.5 Hz, 1H), 2.99 (dd, *J* = 19.0, 13.4 Hz, 1H), 3.69 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.90 (s, 3H), 3.92 (s, 3H), 4.97 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.20 (s, 1H), 6.78 (s, 1H), 6.83 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.99–7.05 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.44–7.50 (m, 3H), 7.81–7.85 (m, 2H), 16.34 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.16 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.5, 36.7 (q, ³J_{C,F} = 1.5 Hz, C-6a), 41.3, 56.0, 56.1, 74.0 (q, ²J_{C,F} = 30.8 Hz, C-6), 85.6, 106.8, 111.1, 112.6, 116.7, 122.3, 123.0, 123.1, 123.4 (q, ¹J_{C,F} = 287.4 Hz, CF₃), 126.2, 127.8 (2C), 128.9 (2C), 129.2, 129.6, 131.4, 136.1, 148.9, 149.1, 149.8, 187.2, 190.4. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₉H₂₅F₃NO₇ 556.1578, found 556.1574.



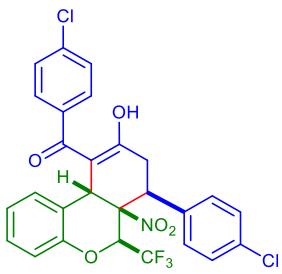
*((6*S**,6*a**R**,7*S**,10*a**R**)-9-Hydroxy-6*a*-nitro-6-(trifluoromethyl)-7-(3,4,5-methoxyphenyl)-6*a*,7,8,10*a*-tetrahydro-6*H*-benzo[*c*]chromen-10-yl)(phenyl)methanone (**5aj**).* Obtained from **1a** (61 mg) and **3j** (85 mg) according to the general procedure. Yield 125 mg (85%), light-yellow powder, mp 171–172 °C. IR (ATR): 1592, 1552, 1484, 1452, 1372, 1257 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 2.73 (dd, *J* = 19.0, 5.5 Hz, 1H), 2.98 (dd, *J* = 19.0, 13.4 Hz, 1H), 3.66 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.87 (s, 6H), 3.91 (s, 3H), 5.01 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.21 (s, 1H), 6.48 (s, 2H), 6.98–7.05 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.43–7.51 (m, 3H), 7.80–7.86 (m, 2H), 16.34 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.21 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 36.8 (q, ³J_{C,F} = 1.1 Hz, C-6a), 41.9, 56.4 (2C), 61.1, 74.0 (q, ²J_{C,F} 31.1 Hz, C-6), 85.7, 106.8, 107.1 (2C), 116.7, 123.0, 123.2, 123.4 (q, ¹J_{C,F} = 287.7 Hz, CF₃), 127.8 (2C), 128.9 (2C), 129.2, 129.3, 129.6, 131.4, 136.1, 139.0, 149.1, 153.3 (2C), 187.0, 190.5. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₀H₂₇F₃NO₈ 586.1683, found 586.1686.



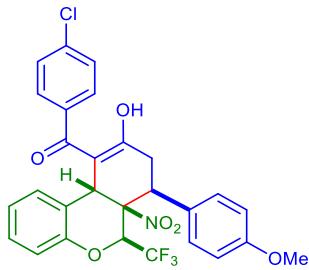
((6S,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-hydroxy-3-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ak).* Obtained from **1a** (61 mg) and **3k** (74 mg) according to the general procedure. Yield 134 mg (98%), yellow powder, mp 127–128 °C. IR (ATR): 3505, 1610, 1585, 1520, 1487, 1454, 1376, 1250 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.72 (dd, *J* = 18.9, 5.3 Hz, 1H), 2.97 (dd, *J* = 18.9, 13.5 Hz, 1H), 3.67 (dd, *J* = 13.5, 5.3 Hz, 1H), 3.92 (s, 3H), 4.98 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.19 (s, 1H), 5.72 (s, 1H), 6.73 (s, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.97–7.12 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 3H), 7.79–7.86 (m, 2H), 16.34 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.16 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 36.7 (br. s, C-6a), 41.4, 56.2, 74.0 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.7, 106.8, 111.7, 114.5, 116.8, 122.9, 123.1, 123.2, 123.4 (q, ¹J_{C,F} = 287.3 Hz, CF₃), 125.7, 127.8 (2C), 128.9 (2C), 129.2, 129.5, 131.4, 136.1, 146.5, 146.6, 149.1, 187.2, 190.4. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₃F₃NO₇ 542.1421, found 542.1412.



((6S,6aS*,7S*,10aR*)-7-(Furan-2-yl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5al).* Obtained from **1a** (61 mg) and **3l** (60 mg) according to the general procedure. Yield 118 mg (97%), white powder, mp 159–160 °C. IR (ATR): 1610, 1603, 1585, 1553, 1485, 1455, 1375, 1279 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.81 (dd, *J* = 19.3, 5.8 Hz, 1H), 3.03 (dd, *J* = 19.3, 13.2 Hz, 1H), 3.85 (dd, *J* = 13.2, 5.8 Hz, 1H), 5.21 (s, 1H), 5.34 (q, ³J_{H,F} = 7.1 Hz, 1H), 6.40 (d, *J* = 2.9 Hz, 1H), 6.43–6.50 (m, 1H), 6.94–7.07 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.42–7.50 (m, 3H), 7.51 (s, 1H), 7.80–7.87 (m, 2H), 16.36 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 90.72 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 32.9, 36.0, 36.2 (q, ³J_{C,F} = 1.4 Hz), 74.2 (q, ²J_{C,F} = 31.3 Hz), 84.7, 106.4, 110.7, 111.0, 117.0, 122.6, 123.1, 123.3 (q, ¹J_{C,F} = 287.3 Hz), 127.8 (2C), 128.9 (2C), 129.0, 129.5, 131.4, 136.1, 143.6, 148.4, 149.2, 185.8, 191.0. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₂₅H₁₈F₃NNaO₆ 508.0978, found 508.0979.

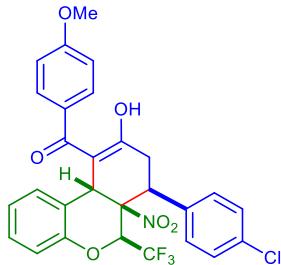


(4-Chlorophenyl)((6S,6aR*,7S*,10aR*)-7-(4-chlorophenyl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5am).* Obtained from **1a** (61 mg) and **3m** (80 mg) according to the general procedure. Yield 131 mg (93%), white powder, mp 212–213 °C. IR (ATR): 1612, 1585, 1551, 1495, 1456, 1369, 1264 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.0, 5.5 Hz, 1H), 2.99 (dd, *J* = 19.0, 13.4 Hz, 1H), 3.72 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.88 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.13 (s, 1H), 6.99–7.05 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.25–7.30 (m, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 16.20 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.00 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.2, 36.7 (q, ³J_{C,F} = 1.3 Hz, C-6a), 41.0, 74.0 (q, ²J_{C,F} = 31.2 Hz, C-6), 85.4, 106.7, 117.1, 122.6, 123.2 (q, ¹J_{C,F} = 287.7 Hz, CF₃), 123.3, 128.9, 129.1 (2C), 129.3 (2C), 129.3 (2C), 129.8, 131.1 (2C), 132.5, 134.4, 135.5, 137.8, 148.9, 186.6, 189.4. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₁₉Cl₂F₃NO₅ 564.0587, found 564.0578.

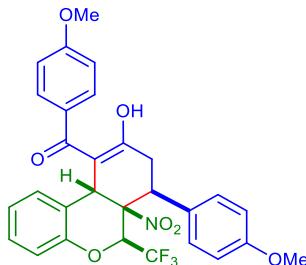


(4-Chlorophenyl)((6S,6aR*,7S*,10aR*)-9-hydroxy-7-(4-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5an).* Obtained from **1a** (61 mg) and **3n** (79 mg) according to the general procedure. Yield 131 mg (93%), white powder, mp 230–231 °C. IR (ATR): 1609, 1585, 1548, 1487, 1457, 1367, 1258 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.1, 5.5 Hz, 1H), 2.99 (dd, *J* = 19.1, 13.5 Hz, 1H), 3.69 (dd, *J* = 13.5, 5.5 Hz, 1H), 3.85 (s, 3H), 4.93 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.10 (s, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.98–7.03 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.24–7.29 (m, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 16.22 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.14 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.5, 36.7 (q, ³J_{C,F} = 1.5 Hz, C-6a), 40.9, 55.5, 74.0 (q, ²J_{C,F} = 30.9 Hz, C-6), 85.6, 106.9, 114.2 (2C), 117.0, 122.8, 123.1, 123.4 (q, ¹J_{C,F} = 287.7 Hz, CF₃), 125.8, 128.9, 129.3 (2C), 129.3 (2C), 129.7, 130.8 (2C), 134.5, 137.7, 149.1, 160.3, 187.3, 189.1. HRMS (ESI) *m/z*: [M + H]⁺ calcd for

$C_{28}H_{22}ClF_3NO_6$ 560.1082, found 564.1078.

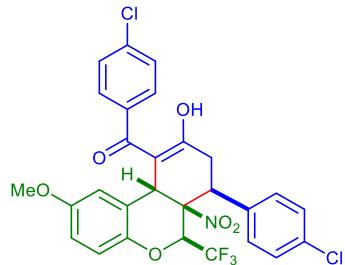


((6S*,6aR*,7S*,10aR*)-7-(4-Chlorophenyl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5ao). Obtained from **1a** (61 mg) and **3o** (79 mg) according to the general procedure. Yield 132 mg (94%), white powder, mp 195–196 °C. IR (ATR): 1607, 1585, 1549, 1490, 1454, 1366, 1252 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.68 (dd, *J* = 18.9, 5.5 Hz, 1H), 2.98 (dd, *J* = 18.9, 13.4 Hz, 1H), 3.71 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.83 (s, 3H), 4.88 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.28 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 7.9, 3.9 Hz, 2H), 7.19–7.28 (m, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 16.42 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.02 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.0, 36.7 (br. s, C-6a), 40.9, 55.5, 73.9 (q, ²J_{C,F} = 31.0 Hz, C-6), 85.5, 106.4, 114.3 (2C), 116.9, 123.0, 123.2 (q, *J* = 287.7 Hz, CF₃), 123.3, 128.5, 129.0 (2C), 129.3, 129.6, 130.0 (2C), 131.1 (2C), 132.7, 135.3, 148.9, 162.2, 185.4, 190.5. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₈H₂₂ClF₃NO₆ 560.1082, found 564.1076.

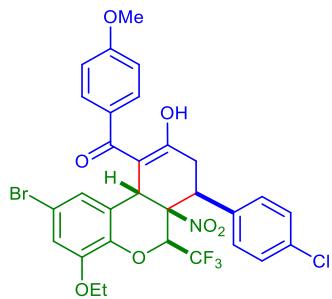


((6S*,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5ap). Obtained from **1a** (61 mg) and **3p** (79 mg) according to the general procedure. Yield 131 mg (94%), yellow powder, mp 189–190 °C. IR (ATR): 1606, 1583, 1553, 1483, 1454, 1370, 1249 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.68 (dd, *J* = 19.1, 5.4 Hz, 1H), 2.98 (dd, *J* = 19.1, 13.5 Hz, 1H), 3.69 (dd, *J* = 13.5, 5.4 Hz, 1H), 3.83 (s, 3H), 3.85 (s, 3H), 4.94 (q, ³J_{H,F} = 7.0 Hz, 1H), 5.25 (s, 1H), 6.90–7.02 (m, 5H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.21–7.26 (m, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 16.43 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.16 (d, *J* = 7.0 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.3, 36.7 (q, ³J_{C,F} = 1.2 Hz, C-6a), 40.8, 55.5, 55.5, 74.0 (q, ²J_{C,F} = 31.1 Hz, C-6), 85.7, 106.6, 114.1 (2C), 114.3 (2C), 116.8, 123.1,

123.2, 123.4 (q, $^1J_{C,F} = 287.3$ Hz, CF₃), 126.0, 128.6, 129.3, 129.5, 130.0 (2C), 130.8 (2C), 149.1, 160.2, 162.1, 186.2, 190.2. HRMS (ESI) m/z : [M + H]⁺ calcd for C₂₉H₂₅F₃NO₇ 556.1578, found 556.1572.

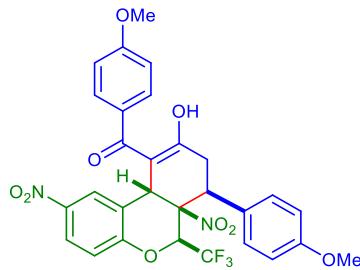


(4-Chlorophenyl)((6S,6aR*,7S*,10aR*)-7-(4-chlorophenyl)-9-hydroxy-2-methoxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5im).* Obtained from **1i** (69 mg) and **3m** (80 mg) according to the general procedure. Yield 136 mg (91%), white powder, mp 187–188 °C. IR (ATR): 1595, 1547, 1492, 1418, 1374, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.71 (dd, $J = 19.0, 5.5$ Hz, 1H), 2.99 (dd, $J = 19.0, 13.5$ Hz, 1H), 3.72 (s, 3H), 3.74 (dd, $J = 13.5, 5.5$ Hz, 1H), 4.83 (q, $^3J_{H,F} = 7.1$ Hz, 1H), 5.14 (s, 1H), 6.49 (d, $J = 2.8$ Hz, 1H), 6.80 (dd, $J = 8.9, 2.8$ Hz, 1H), 6.99 (d, $J = 8.9$ Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 16.24 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.08 (d, $J = 7.1$ Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.1, 36.8 (q, $^3J_{C,F} = 1.4$ Hz, C-6a), 41.0, 55.8, 73.9 (q, $^2J_{C,F} = 31.1$ Hz, C-6), 85.6, 106.7, 114.1, 115.2, 117.8, 123.2 (q, $J = 287.9$ Hz, CF₃), 123.3, 129.1 (2C), 129.3 (2C), 129.4 (2C), 131.1 (2C), 132.6, 134.5, 135.4, 137.9, 142.5, 155.3, 186.7, 189.4. HRMS (ESI) m/z : [M + Na]⁺ calcd for C₂₈H₂₀F₃NNaO₆ 616.0512, found 616.0500.

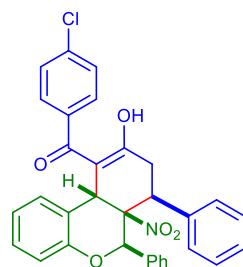


((6S,6aR*,7S*,10aR*)-2-Bromo-7-(4-chlorophenyl)-4-ethoxy-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5fo).* Obtained from **1f** (92 mg) and **3o** (79 mg) according to the general procedure. Yield 157 mg (92%), white powder, mp 214–215 °C. IR (ATR): 1641, 1599, 1556, 1491, 1470, 1423, 1395, 1258 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.45 (t, $J = 7.0$ Hz, 3H), 2.70 (dd, $J = 18.9, 5.6$ Hz, 1H), 2.97 (dd, $J = 18.9, 13.3$ Hz, 1H), 3.68 (dd, $J = 13.3, 5.6$ Hz, 1H), 3.85 (s, 3H), 4.08 (dq, $J = 10.0, 7.0$ Hz, 1H), 4.10 (dq, $J = 10.0, 7.0$ Hz, 1H), 4.95 (q, $^3J_{H,F} = 6.9$ Hz, 1H), 5.24 (s, 1H), 6.74 (d, $J = 1.9$ Hz, 1H), 6.94

(d, $J = 1.9$ Hz, 1H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.8$ Hz, 2H), 16.44 (s, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.17 (d, $J = 6.9$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 14.8, 35.0, 36.6 (q, $^3J_{\text{C},\text{F}} = 1.1$ Hz, C-6a), 41.2, 55.5, 65.7, 73.9 (q, $^2J_{\text{C},\text{F}} = 31.3$ Hz, C-6), 85.3, 106.1, 114.4 (2C), 115.2, 116.7, 123.1 (q, $^1J_{\text{C},\text{F}} = 287.8$ Hz, CF_3), 123.1, 125.5, 128.5, 129.2 (2C), 129.8 (2C), 131.1 (2C), 132.6, 135.4, 138.2, 148.7, 162.3, 185.6, 190.6. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{30}\text{H}_{25}\text{BrClF}_3\text{NO}_7$ 682.0450, found 682.0437.

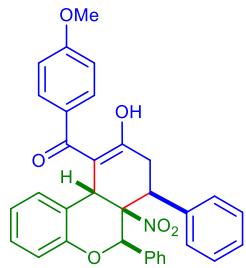


((6S,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-methoxyphenyl)-2,6a-dinitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5gp).* Obtained from **1g** (73 mg) and **3p** (78 mg) according to the general procedure. Yield 145 mg (96%), white powder, mp 234–235 °C. IR (ATR): 1601, 1587, 1549, 1496, 1459, 1373, 1258 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.72 (dd, $J = 19.0, 5.3$ Hz, 1H), 3.02 (dd, $J = 19.0, 13.6$ Hz, 1H), 3.53 (dd, $J = 13.6, 5.3$ Hz, 1H), 3.83 (s, 3H), 3.86 (s, 3H), 5.03 (q, $^3J_{\text{H},\text{F}} = 6.9$ Hz, 1H), 5.33 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 2H), 7.18 (d, $J = 8.9$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 2H), 8.05 (d, $J = 2.4$ Hz, 1H), 8.12 (dd, $J = 8.9, 2.4$ Hz, 1H), 16.52 (s, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.08 (d, $J = 6.9$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.1, 36.5 (br. s, C-6a), 41.0, 55.50, 55.54, 74.5 (q, $^2J_{\text{C},\text{F}} = 31.2$ Hz, C-6), 84.9, 105.6, 114.4 (2C), 114.5 (2C), 117.7, 123.0 (q, $^1J_{\text{C},\text{F}} = 287.5$ Hz, CF_3), 124.4, 125.1, 125.2, 125.7, 128.4, 129.8 (2C), 130.8 (2C), 143.5, 153.8, 160.5, 162.2, 186.1, 191.3. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_9$ 623.1248, found 623.1242.

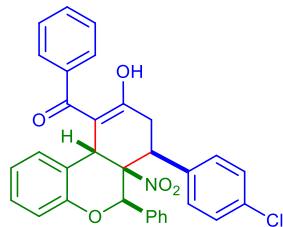


(4-Chlorophenyl)((6S,6aR*,7S*,10aR*)-9-hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5kb).* Obtained from **1k** (64 mg) and **3b** (71 mg) according to the general procedure. Yield 125 mg (93%), white powder, mp 208–209 °C. IR (ATR): 1591, 1580, 1538, 1482, 1449, 1398, 1276, 1225 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.74 (dd, $J = 19.1, 5.4$ Hz,

1H), 3.11 (dd, J = 19.1, 13.5 Hz, 1H), 3.73 (dd, J = 13.5, 5.4 Hz, 1H), 4.97 (s, 1H), 5.45 (s, 1H), 6.83 (d, J = 7.6 Hz, 2H), 6.96–7.01 (m, 2H), 7.09 (d, J = 8.3 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 7.24–7.34 (m, 4H), 7.39–7.47 (m, 5H), 7.59 (d, J = 8.4 Hz, 2H), 16.33 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.5, 35.7, 41.3, 78.1, 91.1, 106.6, 116.7, 121.8, 123.1, 126.8 (2C), 128.5 (2C), 128.6, 128.7 (2C), 128.8, 128.9 (2C), 129.3 (2C), 129.6, 129.7, 130.2 (2C), 134.8, 135.2, 135.8, 137.3, 151.1, 187.5, 190.3. HRMS (ESI) m/z : [M + Na]⁺ calcd for $\text{C}_{32}\text{H}_{24}\text{ClNNaO}_5$ 560.1235, found 560.1229.

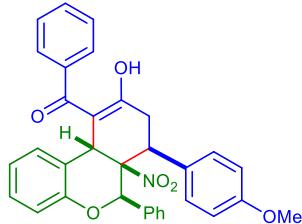


((6S,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5kc).* Obtained from **1k** (64 mg) and **3c** (70 mg) according to the general procedure. Yield 120 mg (90%), white powder, mp 192–193 °C. IR (ATR): 1603, 1580, 1559, 1482, 1449, 1416, 1282, 1227 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.72 (dd, J = 19.0, 5.5 Hz, 1H), 3.10 (dd, J = 19.0, 13.5 Hz, 1H), 3.73 (dd, J = 13.5, 5.5 Hz, 1H), 3.82 (s, 3H), 5.13 (s, 1H), 5.45 (s, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 6.96 (td, J = 7.9, 0.9 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 7.07 (dd, J = 8.1, 0.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 2H), 7.27–7.32 (m, 2H), 7.39–7.47 (m, 5H), 7.64 (d, J = 8.8 Hz, 2H), 16.58 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.5, 35.7, 41.4, 55.5, 78.2, 91.2, 106.4, 113.9 (2C), 116.6, 121.8, 123.5, 127.0 (2C), 128.4 (2C), 128.5, 128.7 (2C), 129.0, 129.2, 129.4 (2C), 129.9 (2C), 130.2 (2C), 135.5, 136.0, 151.1, 161.9, 186.5, 191.2. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{33}\text{H}_{28}\text{NO}_6$ 534.1911, found 534.1903.

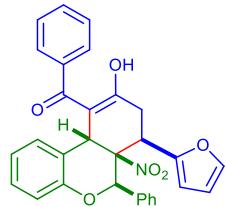


((6S,6aR*,7S*,10aR*)-7-(4-Chlorophenyl)-9-hydroxy-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5ke).* Obtained from **1k** (64 mg) and **3e** (71 mg) according to the general procedure. Yield 131 mg (98%), white powder, mp 206–207 °C. IR (ATR): 1601, 1581, 1547, 1483, 1451, 1410, 1278, 1223 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.72 (dd, J = 19.0, 5.4 Hz, 1H), 3.05 (dd, J = 19.0, 13.5 Hz, 1H), 3.71 (dd, J = 13.5, 5.4 Hz, 1H), 5.07 (s, 1H), 5.39 (s, 1H), 6.83 (d, J = 7.6 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 7.02–7.08 (m, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.27–7.33

(m, 4H), 7.34–7.44 (m, 5H), 7.63 (d, J = 7.6 Hz, 2H), 16.43 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.5, 35.6, 40.9, 78.2, 91.0, 106.5, 116.6, 121.9, 123.2, 126.8 (2C), 127.8 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 129.1, 129.5, 129.6, 131.1, 131.6 (2C), 133.9, 134.6, 135.7, 136.3, 151.0, 186.9, 191.7. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{32}\text{H}_{25}\text{ClNO}_5$ 539.1416, found 538.1415.

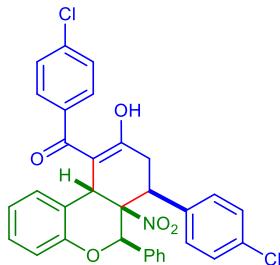


((6S,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-methoxyphenyl)-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5kh).* Obtained from **1k** (64 mg) and **3h** (70 mg) according to the general procedure. Yield 100 mg (75%), white powder, mp 185–186 °C. IR (ATR): 1612, 1603, 1580, 1549, 1484, 1451, 1278, 1226 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.71 (dd, J = 19.2, 5.3 Hz, 1H), 3.05 (dd, J = 19.2, 13.6 Hz, 1H), 3.69 (dd, J = 13.6, 5.3 Hz, 1H), 3.87 (s, 3H), 5.05 (s, 1H), 5.44 (s, 1H), 6.83 (d, J = 7.7 Hz, 2H), 6.93–6.70 (m, 3H), 7.02–7.07 (m, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.23–7.31 (m, 4H), 7.33 (d, J = 8.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 16.44 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.6, 35.9, 40.8, 55.4, 78.2, 91.2, 106.6, 113.8 (2C), 116.5, 121.7, 123.4, 126.9 (2C), 127.2, 127.8 (2C), 128.5 (2C), 128.7 (2C), 129.1, 129.4, 129.4, 131.0, 131.2 (2C), 136.0, 136.4, 151.1, 159.7, 187.5, 191.5. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{33}\text{H}_{28}\text{NO}_6$ 534.1911, found 534.1912.

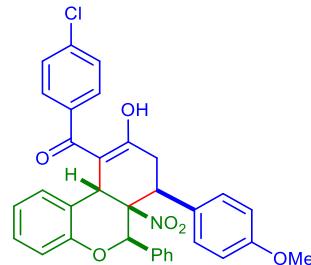


((6R,6aS*,7S*,10aR*)-7-(Furan-2-yl)-9-hydroxy-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(phenyl)methanone (5kl).* Obtained from **1k** (64 mg) and **3l** (60 mg) according to the general procedure. Yield 100 mg (81%), white powder, mp 183–184 °C. IR (ATR): 1603, 1580, 1545, 1483, 1451, 1361, 1278, 1226 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.83 (dd, J = 19.5, 5.9 Hz, 1H), 3.07 (dd, J = 19.5, 13.2 Hz, 1H), 3.86 (dd, J = 13.2, 5.9 Hz, 1H), 5.02 (s, 1H), 5.82 (s, 1H), 6.46 (d, J = 2.5 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 6.87 (d, J = 7.6 Hz, 2H), 6.94 (t, J = 7.6 Hz, 1H), 6.98–7.05 (m, 2H), 7.16 (t, J = 7.6 Hz, 2H), 7.21–7.34 (m, 4H), 7.40 (t, J = 7.4 Hz, 1H), 7.54 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 16.48 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 33.6, 35.3, 36.0, 78.6, 90.3, 106.2, 110.1, 110.9, 116.7, 121.8, 123.1, 126.8 (2C), 127.7 (2C), 128.5 (2C), 128.7 (2C), 128.9, 129.4 (2C),

131.1, 135.8, 136.3, 143.0, 149.9, 151.4, 186.5, 191.9. HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₀H₂₄NO₆ 494.1598, found 494.1601.

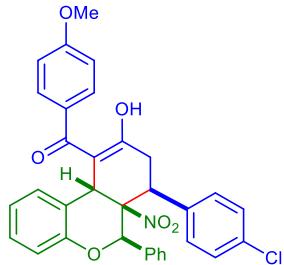


(4-Chlorophenyl)((6S*,6aR*,7S*,10aR*)-7-(4-chlorophenyl)-9-hydroxy-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5km). Obtained from **1k** (64 mg) and **3m** (80 mg) according to the general procedure. Yield 123 mg (86%), white powder, mp 203–204 °C. IR (ATR): 1581, 1544, 1483, 1450, 1399, 1277, 1222 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.72 (dd, *J* = 19.1, 5.5 Hz, 1H), 3.05 (dd, *J* = 19.1, 13.6 Hz, 1H), 3.71 (dd, *J* = 13.6, 5.5 Hz, 1H), 4.97 (s, 1H), 5.39 (s, 1H), 6.83 (d, *J* = 7.7 Hz, 2H), 6.96–7.00 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.25–7.34 (m, 4H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 16.31 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.5, 35.6, 40.8, 78.2, 91.0, 106.4, 116.7, 122.0, 123.0, 126.8 (2C), 128.7 (2C), 128.8 (3C), 128.9 (2C), 129.3 (2C), 129.7, 129.8, 131.5 (2C), 133.8, 134.6, 134.7, 135.6, 137.4, 151.0, 187.0, 190.4. HRMS (ESI) m/z : [M + Na]⁺ calcd for C₃₂H₂₃Cl₂NNaO₅ 594.0845, found 594.0843.

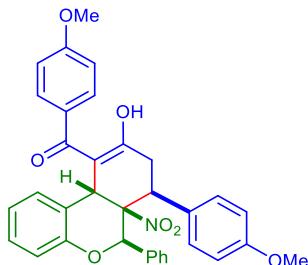


(4-Chlorophenyl)((6R*,6aR*,7S*,10aR*)-9-hydroxy-7-(4-methoxyphenyl)-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)methanone (5kn). Obtained from **1k** (64 mg) and **3n** (79 mg) according to the general procedure. Yield 131 mg (92%), white powder, mp 179–180 °C. IR (ATR): 1593, 1578, 1544, 1482, 1450, 1396, 1278, 1222 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.72 (dd, *J* = 19.2, 5.5 Hz, 1H), 3.05 (dd, *J* = 19.2, 13.6 Hz, 1H), 3.68 (dd, *J* = 13.6, 5.5 Hz, 1H), 3.87 (s, 3H), 4.96 (s, 1H), 5.44 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.93–7.02 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.24–7.36 (m, 6H), 7.59 (d, *J* = 8.4 Hz, 2H), 16.33 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 35.8, 40.7, 55.4, 78.2, 91.2, 106.6, 113.8 (2C), 116.7, 121.8, 123.1, 126.8 (2C), 127.1, 128.7 (2C), 128.8, 128.9 (2C), 129.3 (2C), 129.5, 129.6, 131.2 (2C), 134.8, 135.9, 137.3, 151.1, 159.8,

187.6, 190.2. HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₃H₂₇ClNO₆ 568.1521, found 568.1510.

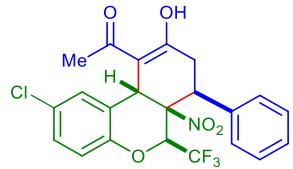


((6R,6aR*,7S*,10aR*)-7-(4-Chlorophenyl)-9-hydroxy-6a-nitro-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5ko).* Obtained from **1k** (64 mg) and **3o** (79 mg) according to the general procedure. Yield 133 mg (94%), white powder, mp 173–174 °C. IR (ATR): 1602, 1581, 1547, 1483, 1450, 1304, 1278, 1222 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 18.9, 5.4 Hz, 1H), 3.04 (dd, *J* = 18.9, 13.5 Hz, 1H), 3.71 (dd, *J* = 13.5, 5.4 Hz, 1H), 3.82 (s, 3H), 5.13 (s, 1H), 5.40 (s, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.27–7.34 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 16.56 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.4, 35.6, 40.8, 55.5, 78.2, 91.1, 106.2, 113.9 (2C), 116.6, 121.9, 123.4, 126.9 (2C), 128.6 (2C), 128.8 (2C), 128.9, 129.2, 129.5, 129.6, 129.9 (2C), 131.6 (2C), 134.0, 134.5, 135.7, 151.0, 161.9, 186.0, 191.3. HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₃H₂₇ClNO₆ 568.1521, found 568.1521.

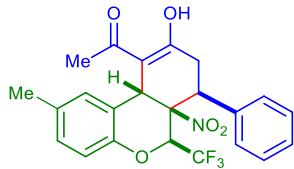


((6R,6aR*,7S*,10aR*)-9-Hydroxy-7-(4-methoxyphenyl)-6a-nitro-6a-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)(4-methoxyphenyl)methanone (5kp).* Obtained from **1k** (64 mg) and **3p** (78 mg) according to the general procedure. Yield 121 mg (86%), beige powder, mp 181–192 °C. IR (ATR): 1601, 1582, 1540, 1482, 1450, 1302, 1278, 1219 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.69 (dd, *J* = 19.0, 5.4 Hz, 1H), 3.04 (dd, *J* = 19.0, 13.6 Hz, 1H), 3.69 (dd, *J* = 13.6, 5.4 Hz, 1H), 3.81 (s, 3H), 3.86 (s, 3H), 5.11 (s, 1H), 5.45 (s, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.93–6.99 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.24–7.32 (m, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 16.58 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 35.6, 35.7, 40.7, 55.4, 55.5, 78.2, 91.3, 106.4, 113.8 (2C), 113.9 (2C), 116.5, 121.7, 123.6, 127.0 (2C), 127.3, 128.7 (2C), 129.0, 129.2, 129.4, 129.4, 129.9 (2C), 131.3 (2C), 136.1, 151.1, 159.7, 161.9, 186.6, 191.2.

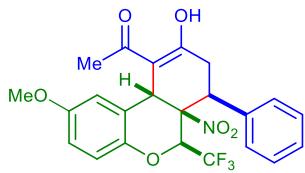
HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₄H₃₀O₇ 564.2017, found 564.2009.



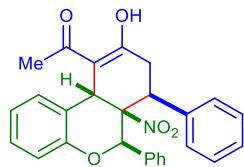
1-((6S,6aR*,7S*,10aR*)-2-Chloro-9-hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)ethan-1-one (5bq).* Obtained from **1b** (70 mg) and **3q** (47 mg) according to the general procedure purified by column chromatography, CH₂Cl₂-hexane (2:1). Yield 113 mg (96%), yellowish powder, mp 112–113 °C. IR (ATR): 1604, 1577, 1554, 1475, 1454, 1371, 1271, 1179 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.48 (s, 3H), 2.66 (dd, *J* = 19.2, 5.6 Hz, 1H), 2.93 (dd, *J* = 19.2, 13.3 Hz, 1H), 3.61 (dd, *J* = 13.3, 5.6 Hz, 1H), 4.73 (s, 1H), 4.89 (q, *J* = 7.1 Hz, 1H), 6.98 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.23–7.26 (m, 2H), 7.30 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.40–7.44 (m, 3H), 16.19 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 90.85 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 24.1, 34.2, 36.8, 41.7, 73.9 (q, *J* = 31.1 Hz), 85.0, 106.7, 118.6, 123.2 (q, *J* = 287.4 Hz), 124.2, 128.55, 128.64, 128.8 (2C), 129.4, 129.86 (2C), 129.93, 133.8, 147.9, 183.0, 195.5. HRMS (ESI) m/z : [M + H]⁺ calcd for C₂₂H₁₈ClF₃NO₅ 468.0826, found 468.0827.



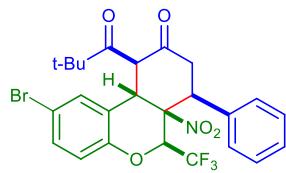
1-((6S,6aR*,7S*,10aR*)-9-Hydroxy-2-methyl-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)ethan-1-one (5hq).* Obtained from **1h** (65 mg) and **3q** (47 mg) according to the general procedure purified by column chromatography, CH₂Cl₂-hexane (2:1). Yield 105 mg (93%), white powder, mp 163–164 °C. IR (ATR): 1616, 1591, 1553, 1493, 1419, 1372, 1269, 1181 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.32 (s, 3H), 2.49 (s, 3H), 2.62 (dd, *J* = 19.2, 5.6 Hz, 1H), 2.92 (dd, *J* = 19.2, 13.3 Hz, 1H), 3.67 (dd, *J* = 13.3, 5.6 Hz, 1H), 4.73 (s, 1H), 4.86 (q, *J* = 7.2 Hz, 1H), 6.78 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.26–7.30 (m, 2H), 7.37–7.44 (m, 3H), 16.13 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 90.83 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 21.0, 24.3, 34.1, 36.8, 41.6, 73.8 (q, *J* = 30.8 Hz), 85.5, 107.4, 117.0, 122.0, 123.4 (q, *J* = 287.6 Hz), 128.7 (2C), 128.9, 129.2, 129.9 (2C), 132.4, 132.8, 134.2, 147.0, 182.3, 196.1. HRMS (ESI) m/z : [M + H]⁺ calcd for C₂₃H₂₁F₃NO₅ 448.1372, found 448.1378.



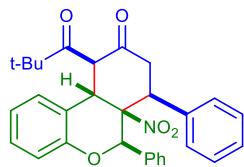
1-((6S,6aR*,7S*,10aR*)-9-Hydroxy-2-methoxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)ethan-1-one (5iq).* Obtained from **1i** (69 mg) and **3q** (47 mg) according to the general procedure purified by column chromatography, CH₂Cl₂-hexane (2:1). Yield 96 mg (83%), white powder, mp 97–98 °C. IR (ATR): 1614, 1552, 1493, 1420, 1373, 1273, 1177 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.48 (s, 3H), 2.63 (dd, *J* = 19.2, 5.6 Hz, 1H), 2.92 (dd, *J* = 19.2, 13.3 Hz, 1H), 3.68 (dd, *J* = 13.3, 5.5 Hz, 1H), 3.78 (s, 3H), 4.74 (s, 1H), 4.85 (q, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.27–7.30 (m, 2H), 7.39–7.43 (m, 3H), 16.16 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.88 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 24.1, 34.2, 37.0, 41.7, 55.9, 73.8 (q, *J* = 30.8 Hz), 85.6, 107.3, 114.3, 114.7, 117.9, 123.3, 123.4 (q, *J* = 287.7 Hz), 128.7 (2C), 129.2, 129.9 (2C), 134.2, 143.0, 155.4, 182.8, 195.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁F₃NO₆ 464.1321, found 464.1332.



1-((6R,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)ethan-1-one (5kq).* Obtained from **1k** (63 mg) and **3q** (47 mg) according to the general procedure purified by column chromatography, CH₂Cl₂-hexane (2:1). Yield 100 mg (91%), yellowish powder, mp 188–189 °C. IR (ATR): 1604, 1581, 1544, 1484, 1451, 1355, 1278, 1188 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.31 (s, 3H), 2.64 (dd, *J* = 19.2, 5.5 Hz, 1H), 3.01 (dd, *J* = 19.2, 13.4 Hz, 1H), 3.67 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.57 (s, 1H), 5.45 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.35–7.46 (m, 6H), 16.12 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 24.3, 34.5, 35.9, 41.6, 78.1, 91.2, 107.3, 116.9, 122.1, 123.0, 126.7 (2C), 128.4 (2C), 128.6, 128.7, 128.8 (2C), 129.5, 129.7, 130.4 (2C), 135.4, 136.0, 151.5, 182.5, 197.1. Anal. Calcd for C₂₇H₂₃NO₅·0.66H₂O: C, 71.51; H, 5.41; N, 3.09. Found: C, 71.54; H, 5.01; N, 3.08. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₄NO₅ 442.1654, found 442.1651.



(6S*,6aR*,7S*,10R*,10aS*)-2-Bromo-6a-nitro-7-phenyl-10-pivaloyl-6-(trifluoromethyl)-6,6a,7,8,10,10a-hexahydro-9H-benzo[c]chromen-9-one (5dr). Obtained from **1d** (81 mg) and **3r** (58 mg) according to the general procedure, purified by column chromatography, CH₂Cl₂-hexane (2:1). Yield 125 mg (90%), white powder, mp 172–173 °C. IR (ATR): 1729, 1690, 1556, 1479, 1457, 1368, 1265, 1169, 1152 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.22 (s, 9H), 2.81 (dd, *J* = 18.3, 9.7 Hz, 1H), 2.89 (dd, *J* = 18.3, 7.0 Hz, 1H), 4.12 (dd, *J* = 9.7, 7.0 Hz, 1H), 4.29 (d, *J* = 8.7 Hz, 1H), 4.95 (q, *J* = 6.8 Hz, 1H), 5.04 (d, *J* = 8.7 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 7.23–7.26 (m, 2H), 7.35 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.41–7.44 (m, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ 95.89 (d, *J* = 6.8 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 26.9 (3C), 37.9, 41.6, 45.1, 45.7, 61.9, 74.5 (q, *J* = 32.3 Hz), 87.6, 116.3, 119.4, 123.1 (q, *J* = 287.1 Hz), 125.4, 129.2 (2C), 129.69, 129.72 (2C), 131.4, 132.5, 133.7, 148.8, 201.9, 211.6. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₂₅H₂₃BrF₃NNaO₅ 576.0604, found 576.0630.

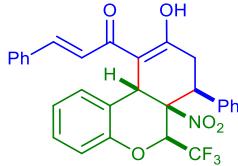


(6S*,6aR*,7S*,10R*,10aS*)-6a-Nitro-6,7-diphenyl-10-pivaloyl-6,6a,7,8,10,10a-hexahydro-9H-benzo[c]chromen-9-one (5kr). Obtained from **1k** (63 mg) and **3r** (58 mg) in CH₂Cl₂ at 35 °C within 16 h. Purified by washing with hexane. Yield 108 mg (89%), white powder, mp 163–164 °C. IR (ATR): 1730, 1698, 1592, 1541, 1492, 1454, 1366, 1258, 1240, 1159 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.04 (s, 9H), 2.88 (dd, *J* = 16.1, 4.0 Hz, 1H), 3.25 (dd, *J* = 16.1, 7.0 Hz, 1H), 3.88 (dd, *J* = 7.0, 4.0 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 5.09 (d, *J* = 11.1 Hz, 1H), 5.94 (s, 1H), 6.86–6.91 (m, 2H), 6.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.03–7.07 (m, 2H), 7.15 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.25–7.31 (m, 3H), 7.45–7.53 (m, 5H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 26.1 (3C), 39.9, 44.0, 45.8, 46.6, 62.7, 77.7, 90.9, 117.3, 122.2, 122.4, 128.38 (2C), 128.42 (2C), 128.7, 129.06 (2C), 129.12, 129.4 (2C), 129.8, 129.9, 134.8, 136.7, 152.1, 203.9, 211.4. Anal. Calcd for C₃₀H₂₉NO₅: C, 74.52; H, 6.05; N, 2.90. Found: C, 74.73; H, 6.20; N, 2.84.

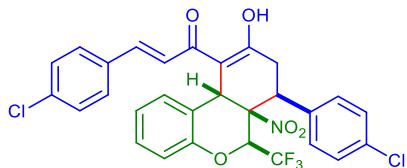
General procedure for the synthesis of 10-cinnamoylhexahydro-9H-benzo[c]chromen-9-ones 6.

A mixture of the appropriate 2*H*-nitrochromene **1** (0.25 mmol), curcuminoid **4** (0.25 mmol) and Cs₂CO₃ (20 mg, 0.06 mmol) was dissolved in dichloromethane (3 mL) and stirred at room temperature (TLC control, CH₂Cl₂-hexane (1:1)) for time period specified in table 2. Upon completion of the reaction,

formed orange solution was quenched with hexane (4 ml), precipitate was filtered off and the residue was evaporated under reduced pressure to complete dryness. Residue was purified as indicated below to give target products **6**.

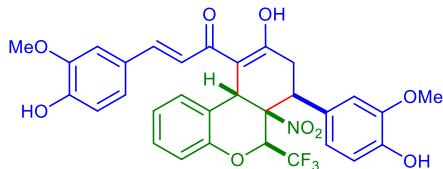


(E)-1-((6S,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-7-phenyl-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)-3-phenylprop-2-en-1-one (6a).* Obtained from **1a** (61 mg) and **4a** (69 mg) according to the general procedure and recrystallized from MeOH. Yield 115 mg (97%), light-yellow powder, mp 210–211 °C. IR (ATR): 1625, 1584, 1549, 1487, 1454, 1371, 1280, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.1, 5.5 Hz, 1H), 2.97 (dd, *J* = 19.1, 13.6 Hz, 1H), 3.74 (dd, *J* = 13.6, 5.5 Hz, 1H), 4.95 (q, ³J_{H,F} = 7.1 Hz, 1H), 4.97 (s, 1H), 6.99 (d, *J* = 15.3 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.27–7.31 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.38–7.45 (m, 6H), 7.53–7.59 (m, 2H), 8.05 (d, *J* = 15.3 Hz, 1H), 16.94 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.27 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 36.3 (q, ³J_{C,F} = 1.0 Hz, C-6a), 36.5, 41.6, 73.9 (q, ²J_{C,F} = 30.8 Hz, C-6), 85.5, 106.5, 117.1, 118.1, 122.3, 123.4, 123.5 (q, ¹J_{C,F} = 287.6 Hz, CF₃), 128.7 (2C), 128.8 (2C), 129.2 (2C), 129.3, 129.5, 129.8 (2C), 129.9, 130.9, 134.1, 134.9, 144.4, 149.4, 179.9, 191.7. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₉H₂₃F₃NO₅ 522.1523, found 522.1521.

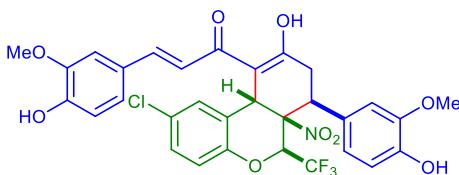


(E)-3-(4-Chlorophenyl)-1-((6S,6aR*,7S*,10aR*)-7-(4-chlorophenyl)-9-hydroxy-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)prop-2-en-1-one (6b).* Obtained from **1a** (61 mg) and **4b** (86 mg) according to the general procedure and recrystallized from MeOH. Yield 140 mg (95%), light-yellow powder, mp 199–200 °C. IR (ATR): 1629, 1587, 1548, 1489, 1453, 1373, 1283, 1267 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.68 (dd, *J* = 19.0, 5.4 Hz, 1H), 2.91 (dd, *J* = 19.0, 13.6 Hz, 1H), 3.72 (dd, *J* = 13.6, 5.4 Hz, 1H), 4.90 (q, ³J_{H,F} = 7.1 Hz, 1H), 4.94 (s, 1H), 6.93 (d, *J* = 15.3 Hz, 1H), 7.04–7.09 (m, 1H), 7.12–7.19 (m, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 15.3 Hz, 1H), 16.88 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.12 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 36.2 (q, ³J_{C,F} = 1.0 Hz, C-6a), 36.4, 41.0, 73.8 (q, ²J_{C,F} = 31.2 Hz, C-6), 85.4, 106.4, 117.2, 118.5, 122.1, 123.3 (q, ¹J = 287.6 Hz, CF₃), 123.6, 129.0 (2C), 129.3, 129.5 (2C), 129.8 (2C), 130.0,

131.2 (2C), 132.5, 133.3, 135.4, 136.9, 143.0, 149.3, 179.6, 191.4. Anal. Calcd for $C_{29}H_{20}Cl_2F_3NO_5 \cdot 1.5H_2O$: C, 56.42; H, 3.76; N, 2.27. Found: C, 56.67; H, 3.49; N, 2.25.

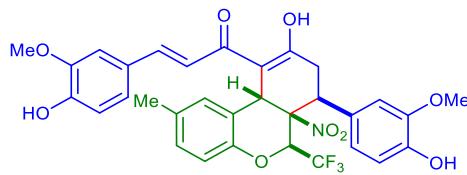


(E)-3-(4-Hydroxy-3-methoxyphenyl)-1-((6S,6aR*,7S*,10aR*)-9-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)prop-2-en-1-one (6c).* Obtained from **1a** (61 mg) and **4c** (92 mg) according to the general procedure and purified by column chromatography (EtOAc-hexane, 1:1). Yield 134 mg (87%), yellow powder, mp 206–207 °C. IR (ATR): 2964, 2924, 1601, 1585, 1549, 1512, 1485, 1454, 1371, 1266 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.68 (dd, *J* = 19.0, 5.4 Hz, 1H), 2.89 (dd, *J* = 19.0, 13.5 Hz, 1H), 3.66 (dd, *J* = 13.5, 5.4 Hz, 1H), 3.90 (s, 3H), 3.92 (s, 3H), 4.93 (s, 1H), 4.99 (q, ³J_{H,F} = 7.2 Hz, 1H), 5.70 (s, 1H), 5.90 (s, 1H), 6.76 (s, 1H), 6.81 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.82 (d, *J* = 15.2 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 1.7 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.12–7.20 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 15.2 Hz, 1H), 17.05 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 91.13 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 36.3 (q, ³J_{C,F} = 1.0 Hz, C-6a), 36.7, 41.5, 56.1, 56.2, 74.0 (q, ²J = 30.9 Hz, C-6), 85.8, 106.2, 110.7, 111.9, 114.4, 115.2, 115.7, 116.9, 122.6, 123.3, 123.4, 123.5, 123.6 (q, ¹J = 287.5 Hz, CF₃), 125.8, 127.6, 129.6, 129.8, 144.6, 146.5, 146.6, 147.0, 148.7, 149.4, 180.9, 190.7. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₁H₂₇F₃NO₉ 614.1632, found 614.1631.

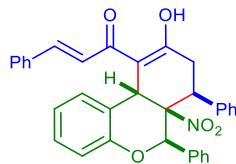


(E)-1-((6S,6aR*,7S*,10aR*)-2-Chloro-9-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)-3-(4-hydroxy-3-methoxyphenyl)-prop-2-en-1-one (6d).* Obtained from **1b** (70 mg) and **4c** (92 mg) according to the general procedure and purified by column chromatography (EtOAc-hexane, 1:1). Yield 137 mg (84%), yellow powder, mp 152–153 °C. IR (ATR): 2921, 2851, 1602, 1552, 1514, 1467, 1455, 1371, 1264 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 19.1, 5.5 Hz, 1H), 2.89 (dd, *J* = 19.1, 13.5 Hz, 1H), 3.61 (dd, *J* = 13.5, 5.5 Hz, 1H), 3.91 (s, 3H), 3.92 (s, 3H), 4.90 (s, 1H), 4.99 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.73 (s, 1H), 5.93 (s, 1H), 6.72 (d, *J* = 1.7 Hz, 1H), 6.77 (d, *J* = 15.2 Hz, 1H), 6.78 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 1.7 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.2 Hz, 1H), 8.01 (d, *J* = 15.2 Hz, 1H), 17.06 (s,

1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.15 (d, $J = 7.1$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 36.3 (q, $^3J_{\text{C},\text{F}} = 1.5$ Hz, C-6a), 36.7, 41.7, 56.1, 74.1 (q, $^2J_{\text{C},\text{F}} = 31.0$ Hz, C-6), 56.2, 85.4, 105.6, 111.0, 111.8, 114.5, 115.1, 115.3, 118.4, 123.3, 123.4 (q, $^1J_{\text{C},\text{F}} = 287.5$ Hz, CF_3), 123.5, 124.5, 125.5, 127.5, 128.7, 129.4 (2C), 130.0, 145.4, 146.6, 147.0, 148.1, 148.9, 180.8, 190.7. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{31}\text{H}_{26}\text{ClF}_3\text{NO}_9$ 648.1243, found 648.1251.

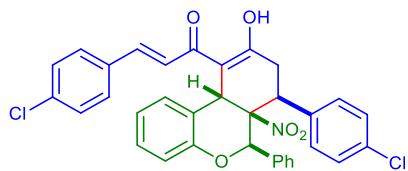


(E)-3-(4-Hydroxy-3-methoxyphenyl)-1-((6S,6aR*,7S*,10aR*)-9-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-2-methyl-6a-nitro-6-(trifluoromethyl)-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)prop-2-en-1-one (6e).* Obtained from **1h** (65 mg) and **4c** (92 mg) according to the general procedure and purified by column chromatography (EtOAc-hexane, 1:1). Yield 130 mg (83%), yellow powder, mp 165–166 °C. IR (ATR): 3502, 3405, 1589, 1552, 1517, 1495, 1452, 1371, 1267 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.24 (s, 3H), 2.67 (dd, $J = 19.0, 5.5$ Hz, 1H), 2.88 (dd, $J = 19.0, 13.5$ Hz, 1H), 3.68 (dd, $J = 13.5, 5.5$ Hz, 1H), 3.91 (s, 6H), 4.91 (s, 1H), 4.96 (q, $^3J_{\text{H},\text{F}} = 7.3$ Hz, 1H), 5.71 (s, 1H), 5.92 (s, 1H), 6.76 (d, $J = 1.7$ Hz, 1H), 6.81 (dd, $J = 8.1, 1.7$ Hz, 1H), 6.83 (d, $J = 15.2$ Hz, 1H), 6.92 (d, $J = 1.4$ Hz, 1H), 6.93 (d, $J = 8.1$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 7.01 (d, $J = 1.7$ Hz, 1H), 7.03 (d, $J = 8.2$ Hz, 1H), 7.11 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.17 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.98 (d, $J = 15.2$ Hz, 1H), 17.05 (s, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.13 (d, $J = 7.3$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 21.0, 36.2 (br. s, C-6a), 36.7, 41.5, 56.1, 56.1, 73.9 (q, $^2J_{\text{C},\text{F}} = 31.0$ Hz, C-6), 85.9, 106.3, 110.8, 111.9, 114.4, 115.2, 115.8, 116.7, 122.2, 123.2, 123.4, 123.6 (q, $^1J_{\text{C},\text{F}} = 287.5$ Hz, CF_3), 125.9, 127.6, 129.8, 130.4, 132.8, 144.6, 146.4, 146.5, 147.0, 147.2, 148.7, 180.9, 190.6. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{32}\text{H}_{29}\text{F}_3\text{NO}_9$ 628.1789, found 628.1781.

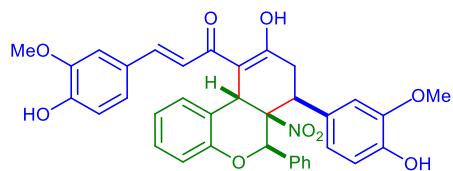


(E)-1-((6R,6aR*,7S*,10aR*)-9-Hydroxy-6a-nitro-6,7-diphenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)-3-phenylprop-2-en-1-one (6f).* Obtained from **1k** (64 mg) and **4a** (69 mg) according to the general procedure and purified by column chromatography (CH_2Cl_2 -hexane, 2:1). Yield 124 mg (94%), light-yellow powder, mp 224–225 °C. IR (ATR): 1629, 1580, 1543, 1483, 1449, 1354, 1274, 1222 cm⁻¹; ^1H NMR (500 MHz, CDCl_3) δ 2.72 (dd, $J = 19.1, 5.4$ Hz, 1H), 3.05 (dd, $J = 19.1, 13.7$ Hz, 1H), 3.76 (dd, $J = 13.7, 5.4$ Hz, 1H), 4.78 (s, 1H), 5.50 (s, 1H), 6.82 (d, $J = 15.4$ Hz, 1H), 7.02–7.07

(m, 3H), 7.16 (d, J = 7.9 Hz, 1H), 7.19 (dd, J = 8.2, 0.8 Hz, 1H), 7.24–7.29 (m, 2H), 7.30–7.40 (m, 5H), 7.40–7.48 (m, 7H), 7.93 (d, J = 15.4 Hz, 1H), 16.90 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.4, 37.0, 41.6, 78.1, 91.0, 106.7, 116.8, 118.6, 122.2, 122.9, 126.8 (2C), 128.4 (2C), 128.5 (2C), 128.6, 128.8 (2C), 129.1 (2C), 129.4, 129.7, 129.8, 130.3 (2C), 130.7, 135.0, 135.4, 136.1, 143.7, 151.6, 180.7, 192.1. Anal. Calcd for $\text{C}_{34}\text{H}_{27}\text{NO}_5$: C, 77.11; H, 5.14; N, 2.64. Found: C, 77.20; H, 5.22; N, 2.83.



(E)-3-(4-Chlorophenyl)-1-((6R,6aR*,7S*,10aR*)-7-(4-chlorophenyl)-9-hydroxy-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)prop-2-en-1-one (6g).* Obtained from **1k** (64 mg) and **4b** (86 mg) according to the general procedure and purified by column chromatography (CH_2Cl_2 -hexane, 2:1). Yield 127 mg (85%), light-yellow powder, mp 154–155 °C. IR (ATR): 1632, 1582, 1549, 1483, 1449, 1358, 1278, 1221 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.70 (dd, J = 19.1, 5.4 Hz, 1H), 2.98 (dd, J = 19.1, 13.7 Hz, 1H), 3.73 (dd, J = 13.7, 5.4 Hz, 1H), 4.74 (s, 1H), 5.45 (s, 1H), 6.75 (d, J = 15.4 Hz, 1H), 7.02–7.08 (m, 3H), 7.13 (dd, J = 7.8, 0.8 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.27 (m, 2H), 7.31–7.45 (m, 10H), 7.87 (d, J = 15.4 Hz, 1H), 16.82 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.3, 36.9, 41.0, 78.1, 90.9, 106.6, 116.9, 118.9, 122.3, 122.7, 126.7 (2C), 128.7 (2C), 128.9 (2C), 129.3, 129.4 (2C), 129.6 (2C), 129.8, 130.0, 131.6 (2C), 133.4, 133.9, 134.6, 135.8, 136.7, 142.3, 151.5, 180.3, 191.9. Anal. Calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{NO}_5$: C, 68.24; H, 4.21; N, 2.34. Found: C, 68.00; H, 4.12; N, 2.28.



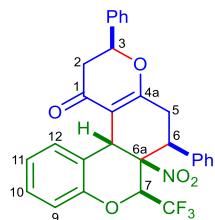
(E)-3-(4-Hydroxy-3-methoxyphenyl)-1-((6R,6aR*,7S*,10aR*)-9-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-6a-nitro-6-phenyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-10-yl)prop-2-en-1-one (6h).* Obtained from **1k** (64 mg) and **4c** (92 mg) according to the general procedure and purified by column chromatography (EtOAc -hexane, 2:3). Yield 137 mg (88%), yellow powder, mp 171–172 °C. IR (ATR): 3501, 3389, 1601, 1582, 1544, 1512, 1484, 1450, 1267 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.70 (dd, J = 19.0, 5.4 Hz, 1H), 2.96 (dd, J = 19.0, 13.7 Hz, 1H), 3.69 (dd, J = 13.7, 5.4 Hz, 1H), 3.89 (s, 3H), 3.94 (s, 3H), 4.73 (s, 1H), 5.54 (s, 1H), 5.71 (s, 1H), 5.90 (s, 1H), 6.65 (d, J = 15.3 Hz, 1H), 6.89–6.93 (m, 2H), 6.94–6.97 (m, 3H), 7.02–7.08 (m, 4H), 7.16 (dd, J = 7.5, 5.1 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.86 (d, J = 15.3 Hz, 1H), 16.96 (s, 1H);

$^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 35.4, 37.2, 41.4, 56.0, 56.1, 78.1, 91.2, 106.4, 110.2, 112.6, 114.2, 115.1, 116.1, 116.6, 122.2, 123.2, 123.3, 123.6, 126.9 (2C), 127.2, 127.7, 128.7 (2C), 129.5, 129.6, 129.8, 136.3, 143.9, 145.9, 146.3, 146.9, 148.5, 151.6, 181.4, 191.1. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{36}\text{H}_{32}\text{NO}_9$ 622.2072, found 622.2069.

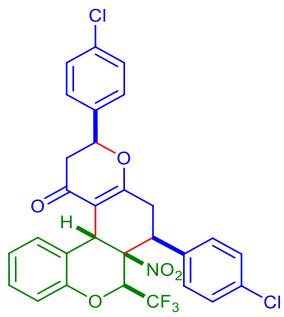
General procedure for the synthesis of 1*H*,6*H*-hexahydrochromeno[6,5-*c*]chromen-1-ones 7

Method A. A mixture of the appropriate 10-cinnamoylhexahydro-9*H*-benzo[*c*]chromen-9-one **6** (0.25 mmol) and Cs_2CO_3 (20 mg, 0.06 mmol) was dissolved in chloroform (3 mL) and refluxed for 48 h (TLC control). Precipitate was filtered off and the residue was evaporated under reduced pressure to complete dryness. Residue was purified by column chromatography with eluent specified below to give target products **7**.

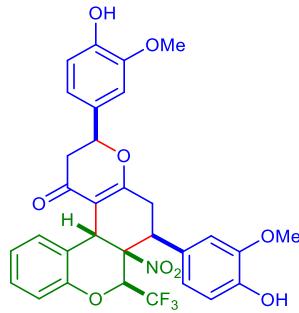
Method B. A mixture of the appropriate 2*H*-nitrochromene **1** (0.25 mmol), curcuminoid **4** (0.25 mmol) and Cs_2CO_3 (20 mg, 0.06 mmol) was dissolved in chloroform (3 mL) and refluxed for 72 h (TLC control). Upon completion of the reaction formed dark solution was quenched with hexane (4 ml), precipitate was filtered off and the residue was evaporated under reduced pressure to complete dryness. Residue was purified by column chromatography with eluent specified below to give target products **7**.



(*3S*,6S*,6aR*,7S*,12bR**)-6*a*-Nitro-3,6-diphenyl-7-(trifluoromethyl)-2,3,5,6*a*,7,12*b*-hexahydro-1*H*,6*H*-chromeno[6,5-*c*]chromen-1-one (**7a**). Obtained according to the general procedure **A** from **6a** (131 mg) or according to the general procedure **B** from **1a** (61 mg) and **4a** (69 mg) and purified by column chromatography (CH_2Cl_2 -hexane, 2:1). Yield 89 mg (68%), white powder, mp 168–169 °C. IR (ATR): 1665, 1615, 1585, 1549, 1487, 1454, 1373, 1309, 1272 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.58 (dd, $J = 18.8, 5.5$ Hz, 1H), 2.92 (dd, $J = 17.3, 3.2$ Hz, 1H), 2.99 (dd, $J = 18.8, 13.1$ Hz, 1H), 3.08 (dd, $J = 17.3, 15.0$ Hz, 1H), 3.77 (dd, $J = 13.1, 5.5$ Hz, 1H), 4.89 (q, $^3J_{\text{H},\text{F}} = 7.2$ Hz, 1H), 5.09 (s, 1H), 5.43 (dd, $J = 15.0, 3.2$ Hz, 1H), 7.10 (dd, $J = 14.6, 7.3$ Hz, 2H), 7.27–7.33 (m, 4H), 7.39–7.47 (m, 8H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.69 (d, $J = 7.2$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.2, 33.8 (q, $^3J_{\text{C},\text{F}} = 1.0$ Hz, C-6a), 42.3, 42.8, 73.7 (q, $^2J_{\text{C},\text{F}} = 31.2$ Hz, C-7), 80.2, 85.2, 113.2, 116.7, 123.3 (q, $^1J_{\text{C},\text{F}} = 287.8$ Hz, CF_3), 123.5, 123.6, 126.5 (2C), 128.8 (2C), 129.1, 129.1 (2C), 129.3, 129.3, 129.8, 129.9 (2C), 134.2, 137.5, 148.8, 169.3, 191.2. HRMS (ESI) m/z : [M + Na]⁺ calcd for $\text{C}_{29}\text{H}_{22}\text{F}_3\text{NNaO}_5$ 544.1342, found 544.1335.

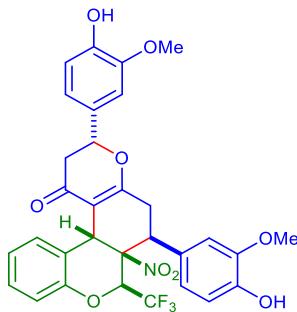


(3S,6S*,6aR*,7S*,12bR*)-3,6-Bis(4-chlorophenyl)-6a-nitro-7-(trifluoromethyl)-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7b).* Obtained according to the general procedure **A** from **6b** (148 mg) or according to the general procedure **B** from **1a** (61 mg) and **4b** (86 mg) and purified by column chromatography (CH_2Cl_2 -hexane, 2:1). Yield 120 mg (81%), white powder, mp 258–259 °C. IR (ATR): 1672, 1622, 1557, 1494, 1454, 1370, 1314, 1273 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.56 (dd, $J = 18.8, 5.4$ Hz, 1H), 2.87–2.96 (m, 2H), 3.03 (dd, $J = 17.3, 14.8$ Hz, 1H), 3.74 (dd, $J = 13.1, 5.4$ Hz, 1H), 4.84 (q, $^3J_{\text{H},\text{F}} = 7.1$ Hz, 1H), 5.08 (s, 1H), 5.41 (dd, $J = 14.8, 3.3$ Hz, 1H), 7.09 (dd, $J = 14.0, 7.3$ Hz, 2H), 7.22–7.26 (m, 2H), 7.26–7.32 (m, 2H), 7.35–7.44 (m, 6H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.51 (d, $J = 7.1$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.1, 33.7 (q, $^3J_{\text{C},\text{F}} = 1.2$ Hz, C-6a), 41.8, 42.8, 73.6 (q, $^2J_{\text{C},\text{F}} = 31.3$ Hz, C-7), 79.5, 85.1, 113.3, 116.8, 123.2 (q, $J = 287.4$ Hz, CF_3), 123.4, 123.6, 127.8 (2C), 129.0 (2C), 129.2, 129.4 (2C), 129.8, 131.2 (2C), 132.6, 135.3, 135.5, 135.9, 148.6, 168.7, 190.7. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{29}\text{H}_{20}\text{Cl}_2\text{F}_3\text{NNaO}_5$ 590.0743, found 590.0747.

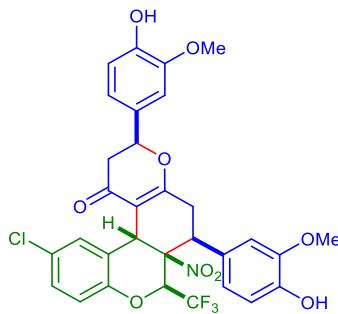


(3S,6S*,6aR*,7S*,12bR*)-3,6-Bis(4-hydroxy-3-methoxyphenyl)-6a-nitro-7-(trifluoromethyl)-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7c).* Obtained according to the general procedure **A** from **6c** (154 mg) or according to the general procedure **B** from **1a** (61 mg) and **4c** (92 mg) as a 81:19 mixture with **7c** and purified by column chromatography (EtOAc -hexane, 1:1) but was not obtained in pure form. Yield 94 mg (61%), yellow powder, mp 170–171 °C. IR (ATR): 2970, 2940, 1664, 1617, 1551, 1518, 1487, 1453, 1370, 1271 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.56 (dd, $J = 19.1, 5.4$ Hz, 1H), 2.88 (dd, $J = 17.2, 3.1$ Hz, 1H), 2.89 (dd, $J = 19.1, 12.9$ Hz, 1H), 3.08 (dd, $J = 17.2, 15.0$ Hz, 1H), 3.69 (dd, $J = 12.9, 5.4$ Hz, 1H), 3.90 (s, 3H), 3.95 (s, 3H), 4.94 (q, $^3J_{\text{H},\text{F}} = 7.2$ Hz, 1H), 5.07 (s, 1H), 5.34 (dd, $J = 15.0, 3.1$ Hz, 1H), 5.72 (s, 1H), 5.73 (s, 1H), 6.76 (s, 1H), 6.90–6.98 (m, 5H),

7.06–7.11 (m, 2H), 7.26–7.31 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.65 (d, $J = 7.2$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (151 MHz, CDCl_3) δ 31.5, 33.7 (q, $^1J_{\text{C},\text{F}} = 0.8$ Hz, C-6a), 42.2, 42.7, 56.1, 56.2, 73.61 (q, $^2J_{\text{C},\text{F}} = 31.0$ Hz, C-7), 80.4, 85.3, 109.0, 113.1, 114.5, 114.7, 116.6, 120.2, 123.3 (q, $^1J_{\text{C},\text{F}} = 287.8$ Hz, CF_3), 123.2, 123.4, 123.6, 125.7, 129.1, 129.2, 129.5, 129.8, 146.5 (2C), 146.7, 147.0, 148.7, 169.5, 191.5. HRMS (ESI) m/z : [M + Na] $^+$ calcd for $\text{C}_{31}\text{H}_{27}\text{F}_3\text{NO}_9$ 614.1632, found 614.1632.

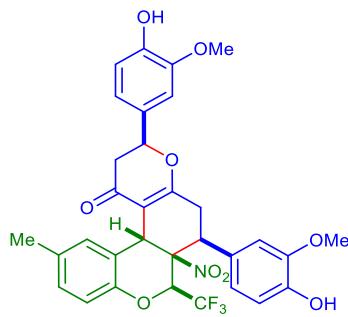


(3R,6S*,6aR*,7S*,12bR*)-3,6-Bis(4-hydroxy-3-methoxyphenyl)-6a-nitro-7-(trifluoromethyl)-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7c).* Obtained as a 19:81 mixture with **7c** and was not isolated in pure form. ^1H NMR (500 MHz, CDCl_3) δ 2.58 (dd, $J = 19.3, 5.8$ Hz, 1H), 2.79 (dd, $J = 19.3, 13.1$ Hz, 1H), 2.97 (dd, $J = 16.4, 4.1$ Hz, 1H), 3.21 (dd, $J = 16.4, 11.6$ Hz, 1H), 3.60 (dd, $J = 13.1, 5.8$ Hz, 1H), 3.90 (s, 6H), 4.89 (q, $^3J_{\text{H},\text{F}} = 7.1$ Hz, 1H), 5.14 (s, 1H), 5.58 (dd, $J = 11.6, 4.1$ Hz, 1H), 5.69 (s, 1H), 5.71 (s, 1H), 6.79–6.87 (m, 5H), 6.98–7.05 (m, 3H), 7.14–7.19 (m, 1H), 7.24 (d, $J = 8.0$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.61 (d, $J = 7.1$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.9, 33.6, 42.5, 42.8, 56.1 (2C), 73.5 (q, $J = 30.8$ Hz), 81.3, 85.4, 109.1, 112.1, 113.2, 114.4, 114.6, 116.7, 119.8, 123.2, 123.3 (q, $J = 287.8$ Hz), 123.4, 125.7, 129.1, 129.2, 129.5, 129.8, 146.4 (2C), 146.7, 148.7, 146.9, 168.4, 192.0.

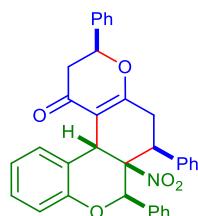


(3S,6S*,6aR*,7S*,12bR*)-11-Chloro-3,6-bis(4-hydroxy-3-methoxyphenyl)-6a-nitro-7-(trifluoromethyl)-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7d).* Obtained according to the general procedure **A** from **6d** (162 mg) or according to the general procedure **B** from **1b** (70 mg) and **4c** (92 mg) as a 91:9 mixture with **7'd** and purified by column chromatography (EtOAc-hexane, 1:1). Yield 117 mg (72%), light-yellow powder, mp 160–161 °C. IR (ATR): 2927, 2851, 1662, 1604, 1552, 1519, 1477, 1455, 1370, 1271 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.59 (dd, $J = 18.9, 5.4$

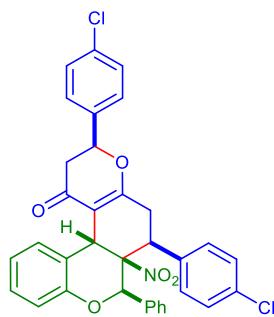
Hz, 1H), 2.85–2.93 (m, 2H), 3.07 (dd, J = 17.3, 15.0 Hz, 1H), 3.62 (dd, J = 13.0, 5.4 Hz, 1H), 3.90 (s, 3H), 3.95 (s, 3H), 4.93 (q, $^3J_{\text{H},\text{F}}$ = 7.1 Hz, 1H), 5.03 (s, 1H), 5.38 (dd, J = 15.0, 3.1 Hz, 1H), 5.72 (s, 1H), 5.73 (s, 1H), 6.73 (s, 1H), 6.77–6.83 (m, 1H), 6.92–6.99 (m, 4H), 7.03 (d, J = 8.4 Hz, 1H), 7.22–7.26 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.67 (d, J = 7.1 Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.5, 33.8 (br. s, C-6a), 42.4, 42.5, 56.1, 56.2, 73.7 (q, $^2J_{\text{C},\text{F}}$ = 31.1 Hz, C-7), 80.4, 85.0, 109.1, 111.7, 112.4, 114.5, 114.8, 118.0, 120.2, 123.2 (q, $^1J_{\text{C},\text{F}}$ = 287.5 Hz, CF_3), 123.4, 125.4, 125.4, 128.6, 129.1, 129.3, 129.6, 146.6, 146.6, 146.7, 147.0, 147.5, 169.8, 191.4. Anal. Calcd for $\text{C}_{31}\text{H}_{25}\text{ClF}_3\text{NO}_9$: C, 57.46; H, 3.89; N, 2.16. Found: C, 57.27; H, 3.92; N, 2.37.



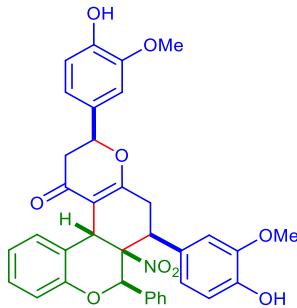
(3S,6S*,6aR*,7S*,12bR*)-3,6-Bis(4-hydroxy-3-methoxyphenyl)-11-methyl-6a-nitro-7-(trifluoromethyl)-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7e).* Obtained according to the general procedure **A** from **6e** (157 mg) or according to the general procedure **B** from **1h** (mg) and **4c** as a 95:5 mixture with **7'e** and purified by column chromatography (EtOAc-hexane, 1:1). Yield 115 mg (73%), yellow powder, mp 172–173 °C. IR (ATR): 3518, 3405, 1663, 1610, 1550, 1519, 1495, 1455, 1370, 1271 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.32 (s, 3H), 2.56 (dd, J = 18.8, 5.4 Hz, 1H), 2.84–2.93 (m, 2H), 3.08 (dd, J = 17.1, 15.0 Hz, 1H), 3.70 (dd, J = 13.0, 5.4 Hz, 1H), 3.90 (s, 3H), 3.95 (s, 3H), 4.90 (q, $^3J_{\text{H},\text{F}}$ = 7.2 Hz, 1H), 5.03 (s, 1H), 5.36 (dd, J = 15.0, 2.9 Hz, 1H), 5.73 (s, 1H), 5.75 (s, 1H), 6.76 (s, 1H), 6.80–6.86 (m, 1H), 6.91–6.99 (m, 5H), 7.03 (s, 1H), 7.07 (d, J = 8.2 Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 91.62 (d, J = 7.2 Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 21.0, 31.6, 33.7 (br. s, C-6a), 42.3, 42.7, 56.1, 56.2, 73.7 (q, $^2J_{\text{C},\text{F}}$ = 31.3 Hz, C-7), 80.2, 85.6, 96.3, 109.1, 112.0, 113.1, 114.5, 114.8, 116.4, 120.3, 123.3, 123.4 (q, $^1J_{\text{C},\text{F}}$ = 288.0 Hz, CF_3), 123.41, 125.8, 129.3, 129.8, 129.8, 132.9, 146.5, 146.6, 146.7, 147.0, 169.4, 191.4. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{32}\text{H}_{29}\text{F}_3\text{NO}_9$ 628.1789, found 628.1785.



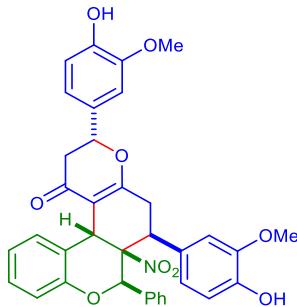
(3S,6S*,6aR*,7R*,12bR*)-6a-Nitro-3,6,7-triphenyl-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7f).* Obtained according to the general procedure A from **6f** (133 mg) or according to the general procedure B from **1k** (64 mg) and **4a** (69 mg) and purified by column chromatography (CH₂Cl₂-hexane, 2:1). Yield 121 mg (91%), white powder, mp 275–276 °C. IR (ATR): 1658, 1605, 1581, 1541, 1484, 1449, 1369, 1278, 1225 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.60 (dd, *J* = 18.9, 5.5 Hz, 1H), 2.85 (dd, *J* = 17.2, 3.3 Hz, 1H), 2.97 (dd, *J* = 17.2, 14.8 Hz, 1H), 3.06 (dd, *J* = 18.9, 13.2 Hz, 1H), 3.81 (dd, *J* = 13.2, 5.5 Hz, 1H), 4.88 (s, 1H), 5.44 (s, 1H), 5.44 (dd, *J* = 14.8, 3.3 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.23–7.29 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.38–7.48 (m, 10H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 31.8, 32.9, 42.4, 42.8, 77.7, 80.2, 90.6, 113.3, 116.6, 122.2, 123.8, 126.4 (2C), 127.2 (2C), 128.4 (2C), 128.6, 128.9 (2C), 129.0 (2C), 129.1, 129.2, 129.3, 129.8, 130.3 (2C), 135.5, 135.6, 137.7, 150.8, 169.9, 191.4. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₄H₂₈NO₅ 530.1962, found 530.1958.



(3S,6S*,6aR*,7R*,12bR*)-3,6-Bis(4-chlorophenyl)-6a-nitro-7-triphenyl-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7g).* Obtained according to the general procedure A from **6g** (150 mg) or according to the general procedure B from **1k** (64 mg) and **4b** (86 mg) and purified by column chromatography (CH₂Cl₂-hexane, 2:1). Yield 132 mg (88%), white powder, mp 272–273 °C. IR (ATR): 1677, 1613, 1584, 1538, 1484, 1450, 1356, 1273, 1224 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.58 (dd, *J* = 18.8, 5.4 Hz, 1H), 2.83 (dd, *J* = 17.2, 3.7 Hz, 1H), 2.92 (dd, *J* = 17.2, 14.4 Hz, 1H), 2.99 (dd, *J* = 18.8, 13.2 Hz, 1H), 3.77 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.86 (s, 1H), 5.38 (s, 1H), 5.41 (dd, *J* = 14.4, 3.7 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 7.12 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.18–7.22 (m, 1H), 7.22–7.29 (m, 2H), 7.30–7.37 (m, 3H), 7.38–7.44 (m, 6H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 31.7, 32.9, 41.9, 42.7, 77.7, 79.4, 90.4, 113.4, 116.7, 122.3, 123.6, 127.1 (2C), 127.8 (2C), 128.7 (2C), 128.9 (2C), 129.3, 129.3 (2C), 129.4, 129.7, 131.6 (2C), 133.9, 134.7, 135.2, 135.2, 136.1, 150.6, 169.4, 190.9. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₄H₂₅Cl₂NNaO₅ 620.1002, found 620.0994.

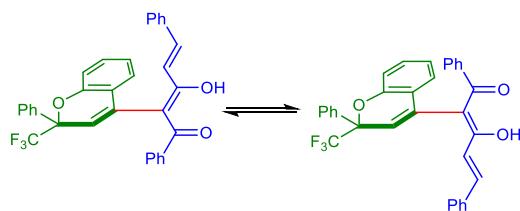


(3S,6S*,6aR*,7R*,12bR*)-3,6-Bis(4-hydroxy-3-methoxyphenyl)-6a-nitro-7-phenyl-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7h).* Obtained according to the general procedure A from **6h** (156 mg) or according to the general procedure **B** from **1k** (64 mg) and **4c** (92 mg) as a 78:22 mixture with **7'h**, purified by column chromatography (EtOAc-hexane, 2:3) but was not obtained in pure form. Yield 86 mg (55%), yellow powder, mp 183–184 °C. IR (ATR): 3509, 3383, 1664, 1604, 1542, 1516, 1485, 1451, 1358, 1271 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.58 (dd, *J* = 18.7, 5.4 Hz, 1H), 2.81 (dd, *J* = 17.1, 3.1 Hz, 1H), 2.92–3.01 (m, 2H), 3.73 (dd, *J* = 13.1, 5.4 Hz, 1H), 3.93 (s, 3H), 3.94 (s, 3H), 4.87 (s, 1H), 5.35 (dd, *J* = 14.8, 3.1 Hz, 1H), 5.47 (s, 1H), 5.69 (s, 1H), 5.70 (s, 1H), 6.89–6.98 (m, 8H), 7.02 (d, *J* = 7.5 Hz, 2H), 7.06–7.10 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.30–7.34 (m, 1H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 32.2, 32.9, 42.3, 42.7, 56.0, 56.2, 77.7, 80.4, 90.7, 109.0, 112.6, 113.2, 114.2, 114.7, 116.5, 120.2, 122.2, 123.9, 127.1, 127.2 (2C), 128.9 (3C), 129.1, 129.3, 129.4, 129.8, 135.6, 145.9, 146.2, 146.6, 146.9, 150.8, 170.0, 191.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₆H₃₂NO₉ 622.2072, found 622.2067.

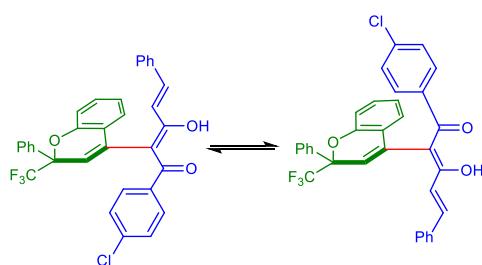


(3R,6S*,6aR*,7R*,12bR*)-3,6-Bis(4-hydroxy-3-methoxyphenyl)-6a-nitro-7-phenyl-2,3,5,6a,7,12b-hexahydro-1H,6H-chromeno[6,5-c]chromen-1-one (7'h).* Was not obtained in pure form. Yield 25 mg (16%), yellow powder. ¹H NMR (500 MHz, CDCl₃) δ 3.17 (dd, *J* = 16.3, 12.0 Hz, 1H), 3.63 (dd, *J* = 13.1, 5.9 Hz, 1H), 3.90 (s, 3H), 3.92 (s, 3H), 4.93 (s, 1H), 5.42 (s, 1H), 5.42–5.46 (m, 1H), 5.68 (s, 2H) (other signals are masked by the isomer **7h**); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 32.6, 32.9, 42.2, 42.5, 56.0, 56.1, 77.8, 81.2, 91.1, 109.1, 112.7, 113.5, 114.1, 114.6, 116.4, 119.8, 121.9, 123.5, 127.1 (2C), 127.1, 129.2, 129.4 (2C), 129.5, 129.7, 135.8, 145.9, 146.2, 146.4, 146.8, 150.9, 169.2, 192.0 (2C are masked by the major isomer).

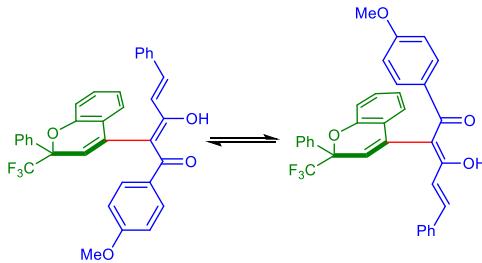
General procedure for the synthesis of trienes 8. A mixture of the appropriate 3-nitro-2-phenyl-2-(trifluoromethyl)-2H-chromene **2** (0.25 mmol), enedione **3** (0.25 mmol) and DABCO (34 mg, 0.3 mmol) was dissolved in chloroform (4 mL) and refluxed for 72 h (TLC control, CH₂Cl₂-hexane (1:1)). Upon completion of the reaction, formed orange solution was evaporated under reduced pressure to complete dryness, triturated with hexane and dried again. Residue was recrystallized from methanol to give target products **8**.



(*2Z,4E*)-3-Hydroxy-1,5-diphenyl-2-(2-phenyl-2-(trifluoromethyl)-2*H*-chromen-4-yl)penta-2,4-dien-1-one (**8a**). Obtained according to the general procedure from **2a** (80 mg) and **3a** (63 mg). Yield 105 mg (80%), yellow powder, mp 165–166 °C. IR (ATR): 1622, 1600, 1575, 1482, 1447 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of 50:50) 6.00 (s, 1H), 6.26 (s, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.96–7.03 (m, 3H), 7.04–7.10 (m, 3H), 7.11–7.42 (m, 26H), 7.56–7.64 (m, 4H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 17.57 (s, 1H), 17.73 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 82.62 (s, CF₃), 82.75 (s, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 80.5 (q, ²J_{C,F} = 30.2 Hz, C-2), 80.6 (q, ²J_{C,F} = 30.2 Hz, C-2), 108.7, 108.9, 116.9, 117.0, 120.7, 121.15, 122.17, 122.19, 122.4, 122.6, 122.8, 123.2, 123.8 (q, ¹J_{C,F} = 284.6 Hz, CF₃), 123.9 (q, ¹J_{C,F} = 284.9 Hz, CF₃), 126.0, 126.4, 126.7 (2C), 126.9 (2C), 127.8 (2C), 128.0 (2C), 128.03 (2C), 128.3 (2C), 128.4 (2C), 128.5 (2C), 128.6 (2C), 128.86 (2C), 128.90 (2C), 128.93, 129.1 (2C), 129.2, 130.4, 130.5, 130.9, 131.0, 131.1, 131.3, 133.4, 133.7, 134.9, 135.1, 135.7, 136.8, 137.0, 137.4, 142.1, 142.5, 151.1, 151.3, 180.5, 182.5, 190.6, 192.2. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₃H₂₄F₃O₃ 525.1672, found 525.1679.

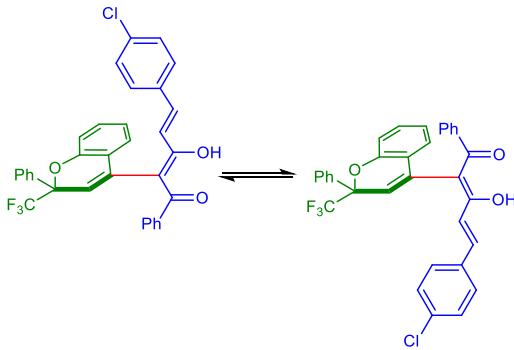


(2Z,4E)-1-(4-Chlorophenyl)-3-hydroxy-5-phenyl-2-(2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)penta-2,4-dien-1-one (8b). Obtained according to the general procedure from **2a** (80 mg) and **3b** (71 mg). Yield 95 mg (68%), light-yellow powder, mp 192–193 °C. IR (ATR): 1625, 1597, 1575, 1482, 1449 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of ≈50:50) 5.98 (s, 1H), 6.28 (s, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.89–6.98 (m, 4H), 7.07–7.37 (m, 24H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.56–7.63 (m, 4H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 17.52 (s, 1H), 17.62 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 82.55 (s, CF₃), 82.79 (s, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 80.5 (q, ²J_{C,F} = 30.1 Hz, C-2), 80.6 (q, ²J_{C,F} = 30.2 Hz, C-2), 108.6, 108.7, 117.11, 117.14, 120.4, 120.8, 121.9, 122.0, 122.6, 122.7, 123.0, 123.4, 123.8 (q, ¹J_{C,F} = 284.5 Hz, 2CF₃), 125.9, 126.2, 126.5 (2C), 126.8 (2C), 128.4 (2C), 128.49 (2C), 128.51 (2C), 128.54 (2C), 128.6 (2C), 128.9 (2C), 128.94 (2C), 129.11 (2C), 129.16, 129.18 (2C), 129.3, 129.5 (2C), 130.5, 130.6, 131.2, 131.3, 133.1, 133.5, 134.8, 135.0, 135.3, 135.5, 135.7, 136.6, 137.2, 137.6, 142.5, 142.9, 151.1, 151.3, 180.7, 182.5, 189.3, 190.5. Anal. Calcd for C₃₃H₂₂ClF₃O₃·1.5H₂O: C, 67.64; H, 4.30. Found: C, 67.75; H, 4.01.

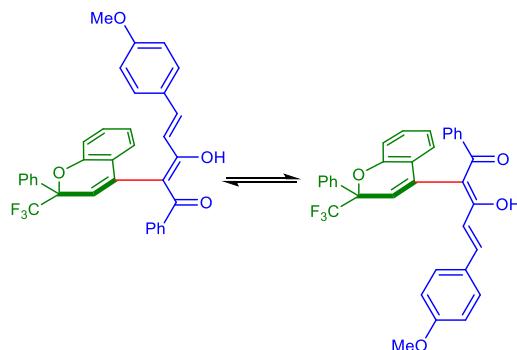


(2Z,4E)-3-Hydroxy-1-(4-methoxyphenyl)-5-phenyl-2-(2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)penta-2,4-dien-1-one (8c). Obtained according to the general procedure from **2a** (80 mg) and **3c** (70 mg). Yield 96 mg (69%), yellow powder, mp 150–151 °C. IR (ATR): 1627, 1604, 1578, 1482, 1448 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of 50:50) 3.71 (s, 3H), 3.78 (s, 3H), 6.05 (s, 1H), 6.30 (s, 1H), 6.41–6.47 (m, 3H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.14–7.45 (m, 22H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 15.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 15.6 Hz, 1H), 17.87 (s, 1H), 17.90 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 82.53 (s, CF₃), 82.85 (s, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 55.3, 55.5, 80.63 (q, ²J_{C,F} = 30.4 Hz, C-2), 80.64 (q, ²J_{C,F} = 30.4 Hz, C-2), 108.2, 108.3, 113.4 (2C), 113.6 (2C), 117.0 (2C), 120.9, 121.2, 122.12, 122.13, 122.16, 122.7, 122.8, 123.0, 123.9 (q, ¹J_{C,F} = 284.1 Hz, 2CF₃), 126.1, 126.5, 126.8 (4C), 128.37 (2C), 128.42 (2C), 128.5 (2C), 128.8 (2C), 128.9, 128.9 (2C), 129.1 (2C), 129.2, 129.3, 129.7, 130.2 (3C), 130.3, 130.7 (2C), 131.0, 131.1, 133.8, 134.1, 135.0, 135.2, 135.7, 136.7, 141.6, 141.9, 151.2, 151.3, 161.9, 162.4, 180.2, 181.4, 190.1, 190.5. HRMS (ESI) *m/z*: [M + H]⁺ calcd

for C₃₄H₂₆F₃O₄ 555.1778, found 555.1776.

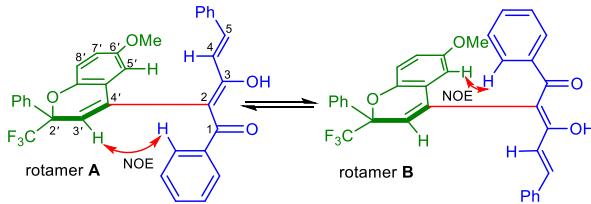


(2Z,4E)-5-(4-Chlorophenyl)-3-hydroxy-1-phenyl-2-(2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)penta-2,4-dien-1-one (8d). Obtained according to the general procedure from **2a** (80 mg) and **3d** (71 mg). Yield 98 mg (70%), yellow powder, mp 153–154 °C. IR (ATR): 1626, 1605, 1569, 1491, 1452 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of ≈50:50) 6.00 (s, 1H), 6.25 (s, 1H), 6.39 (d, J = 15.6 Hz, 1H), 6.68 (d, J = 15.8 Hz, 1H), 6.80 (td, J = 7.6, 0.8 Hz, 1H), 6.90 (td, J = 7.6, 0.8 Hz, 1H), 6.96–7.02 (m, 5H), 7.08 (d, J = 8.0 Hz, 1H), 7.12–7.44 (m, 24H), 7.57–7.62 (m, 4H), 7.67 (d, J = 15.8 Hz, 1H), 7.70 (d, J = 15.8 Hz, 1H), 17.51 (s, 1H), 17.66 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 82.63 (s, 3F), 82.74 (s, 3F); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 80.5 (q, ²J_{C,F} = 30.5 Hz, C-2), 80.6 (q, ²J_{C,F} = 30.7 Hz, c-2), 108.8, 109.0, 117.0 (2C), 121.2, 121.6, 122.0, 122.1, 122.4, 122.6, 122.8, 123.2, 123.7 (q, ¹J_{C,F} J = 284.0 Hz, CF₃), 123.9 (q, ¹J_{C,F} = 284.8 Hz, CF₃), 126.0, 126.3, 126.7 (2C), 126.8 (2C), 127.8 (2C), 128.0 (2C), 128.1 (2C), 128.3 (2C), 128.6 (2C), 128.9 (2C), 129.0, 129.1 (2C), 129.2, 129.4 (2C), 129.5 (2C), 129.6 (2C), 131.0, 131.1 (2C), 131.4, 133.4 (2C), 133.5, 133.6, 135.6, 136.2, 136.4, 136.8, 136.9, 137.3, 140.5, 140.9, 151.1, 151.3, 179.9, 181.9, 190.8, 192.3. HRMS (ESI) m/z: [M + H]⁺ calcd for C₃₃H₂₃ClF₃O₃ 559.1282, found 559.1280.



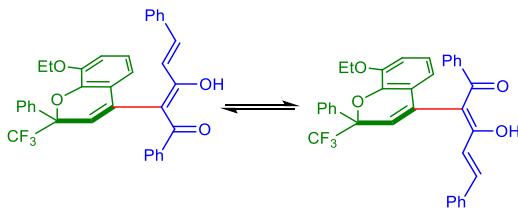
(2Z,4E)-3-Hydroxy-5-(4-methoxyphenyl)-1-phenyl-2-(2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)penta-2,4-dien-1-one (8e). Obtained from **2a** (80 mg) and **3e** (70 mg) according to the general procedure. Yield 95 mg (69%), yellow powder, mp 177–178 °C. IR (ATR): 1622, 1602, 1570, 1510, 1481, 1454 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of 50:50) 3.82

(s, 6H), 5.99 (s, 1H), 6.24 (s, 1H), 6.31 (d, $J = 15.6$ Hz, 1H), 6.58 (d, $J = 15.6$ Hz, 1H), 6.74 (d, $J = 8.5$ Hz, 2H), 6.79 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 6.90 (t, $J = 7.5$ Hz, 1H), 6.96–7.08 (m, 6H), 7.11–7.42 (m, 20H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 15.6$ Hz, 1H), 7.75 (d, $J = 15.6$ Hz, 1H) 17.69 (s, 1H), 17.83 (s, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ 82.63 (s, CF_3), 82.75 (s, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (151 MHz, CDCl_3) δ 55.5 (2C), 80.5 (q, $^2J_{\text{C},\text{F}} = 30.1$ Hz, C-2), 80.6 (q, $^2J_{\text{C},\text{F}} = 30.2$ Hz, C-2), 108.36, 108.43, 114.3 (2C), 114.6 (2C), 116.9 (2C), 118.3, 118.7, 122.2, 122.3 (2C), 122.6, 122.8, 123.1, 123.8 (q, $^1J_{\text{C},\text{F}} = 284.8$ Hz, CF_3), 123.9 (q, $^2J_{\text{C},\text{F}} = 285.2$ Hz, CF_3), 126.1, 126.4, 126.7 (2C), 126.9 (2C), 127.7, 127.8 (2C), 127.9, 127.94 (2C), 128.0 (2C), 128.3 (2C), 128.5 (2C), 128.87 (2C), 128.9, 129.1, 130.2 (2C), 130.3 (2C), 130.8, 130.9, 131.0, 131.1, 133.6, 133.8, 135.7, 136.8, 137.0, 137.4, 142.0, 142.5, 151.1, 151.3, 161.6, 161.7, 181.4, 183.3, 189.6, 191.2. HRMS (ESI) m/z : [M + H]⁺ calcd for $\text{C}_{34}\text{H}_{26}\text{F}_3\text{O}_4$ 555.1778, found 555.1784.



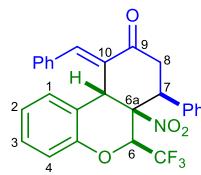
(2Z,4E)-3-Hydroxy-2-(6-methoxy-2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)-1,5-diphenyl-penta-2,4-dien-1-one (8f). Obtained from **2b** (88 mg) and **3a** (63 mg) according to the general procedure. Yield 102 mg (74%), yellow powder, mp 149–150 °C. IR (ATR): 1630, 1578, 1484, 1451 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ (a mixture of two rotamers **A** and **B** in the ratio of 53:47) δ rotamer **A** (53%) 3.60 (s, 3H, OMe), 6.29 (s, 1H, H-3'), 6.45 (d, $J = 15.6$ Hz, 1H, H-5), 6.50 (d, $J = 2.8$ Hz, 1H, H-5'), 6.71 (dd, $J = 8.9, 2.8$ Hz, 1H, H-7'), 7.00 (d, $J = 8.9$ Hz, 1H, H-8'), 7.11 (d, $J = 7.7$ Hz, 2H, H_o Ph-5), 7.19 (t, $J = 7.7$ Hz, 2H, H_m Ph-5), 7.26 (t, $J = 7.7$ Hz, 2H, H_m Ph-2'), 7.28 (t, $J = 7.7$ Hz, 1H, H_p Ph-5), 7.32 (t, $J = 7.7$ Hz, 1H, H_p Ph-2'), 7.34 (t, $J = 7.7$ Hz, 2H, H_m Bz), 7.38 (t, $J = 7.7$ Hz, 1H, H_p Bz), 7.59 (d, $J = 7.7$ Hz, 2H, H_o Ph-2'), 7.61 (d, $J = 7.7$ Hz, 2H, H_o Bz), 7.76 (d, $J = 15.6$ Hz, 1H, H-4), 17.59 (s, 1H, OH); rotamer **B** (47%) 3.64 (s, 3H, OMe), 6.04 (s, 1H, H-3'), 6.68 (d, $J = 2.8$ Hz, 1H, H-5'), 6.73 (d, $J = 15.8$ Hz, 1H, H-5), 6.79 (dd, $J = 8.9, 2.8$ Hz, 1H, H-7'), 7.01 (t, $J = 7.7$ Hz, 2H, H_m Ar), 7.08 (d, $J = 8.9$ Hz, 1H, H-8'), 7.13 (d, $J = 7.7$ Hz, 2H, H_o Ph-2'), 7.24 (t, $J = 7.7$ Hz, 2H, H_m Bz), 7.25 (t, $J = 7.7$ Hz, 2H, H_m Ph-2'), 7.29 (t, $J = 7.7$ Hz, 1H, H_p Ph-2'), 7.34 (t, $J = 7.7$ Hz, 1H, H_p Bz), 7.35 (t, $J = 7.7$ Hz, 1H, H_p Ph-5), 7.39 (d, $J = 7.7$ Hz, 2H, H_o Ph-5), 7.40 (d, $J = 7.7$ Hz, 2H, H_o Bz), 7.78 (d, $J = 15.6$ Hz, 1H, H-4), 17.76 (s, 1H, OH). ^{19}F NMR (376 MHz, CDCl_3) δ 82.66 (s, CF_3), 82.77 (s, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (151 MHz, CDCl_3) δ 29.8, 55.8, 80.4 (q, $^2J_{\text{C},\text{F}} = 30.3$ Hz, C-2), 80.5 (q, $^2J_{\text{C},\text{F}} = 30.0$ Hz, C-2), 108.7, 108.8, 111.0, 111.2, 116.1, 116.3, 117.7, 117.8, 120.7, 121.0, 122.95, 123.02, 123.20, 123.8 (q, $^1J_{\text{C},\text{F}} = 284.5$ Hz, CF_3), 123.9 (q, $^1J_{\text{C},\text{F}} = 286.5$ Hz, CF_3), 124.0, 126.9 (2C), 127.0 (2C), 127.8 (2C), 128.0 (2C), 128.1 (2C), 128.4 (2C), 128.49 (2C), 128.50 (2C), 128.54 (2C), 128.86 (4C), 128.92, 129.1 (2C), 129.2,

130.4, 130.5, 131.0, 131.3, 133.5, 133.7, 134.9, 135.1, 135.5, 136.6, 136.9, 137.4, 142.2, 142.6, 144.9, 145.1, 154.8, 155.0, 180.5, 182.7, 190.4, 192.1. HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₄H₂₆F₃O₄ 555.1778, found 555.1783.

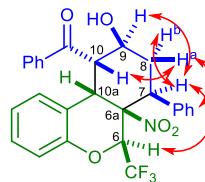


(2Z,4E)-2-(8-Ethoxy-2-phenyl-2-(trifluoromethyl)-2H-chromen-4-yl)-3-hydroxy-1,5-diphenylpent-2,4-dien-1-one (8g). Obtained according to the general procedure from **2c** (91 mg) and **3a** (63 mg). Yield 103 mg (72%), yellow powder, mp 158–159 °C. IR (ATR): 1622, 1598, 1578, 1485, 1449 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (a mixture of two rotamers in the ratio of 50:50) 1.50–1.54 (m, 3H), 1.54–1.58 (m, 3H), 4.07–4.28 (m, 4H), 6.05 (s, 1H), 6.32 (s, 1H), 6.44 (d, J = 15.5 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 6.71 (d, J = 15.7 Hz, 1H), 6.68–6.74 (m, 1H), 6.80 (d, J = 7.6 Hz, 2H), 6.81–6.85 (m, 1H), 6.89 (dd, J = 7.9, 1.2 Hz, 1H), 6.99 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 4.3 Hz, 3H), 7.21–7.41 (m, 19H), 7.61 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 15.9 Hz), 7.77 (d, J = 15.4 Hz, 1H), 17.56 (s, 1H), 17.76 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ 82.70 (s, CF₃), 82.87 (s, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 15.1, 15.2, 65.16, 65.23, 80.67 (q, $^2J_{C,F}$ = 30.3 Hz), 80.77 (q, $^2J_{C,F}$ = 30.2 Hz), 109.0, 109.2, 115.7, 115.9, 118.0, 118.3, 120.8, 121.2, 122.3, 122.5, 122.8, 122.9, 123.70, 123.72, 123.80 (q, $^1J_{C,F}$ = 284.9 Hz), 123.83, 123.83 (q, $^1J_{C,F}$ = 282.4 Hz), 124.7, 126.8 (2C), 126.9 (2C), 127.9 (2C), 128.0 (4C), 128.4 (3C), 128.5 (4C), 128.79 (2C), 128.83 (2C), 128.9, 129.1 (2C), 129.2, 130.3, 130.5, 130.9, 131.2, 133.6, 133.9, 134.9, 135.1, 135.2, 136.4, 136.9, 137.4, 140.6, 142.0, 142.5, 147.7, 147.9, 180.4, 182.8, 190.3, 192.2. HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₅H₂₈F₃O₄ 569.1934, found 569.1935.

Procedure for the reduction of compound 5aa. To a stirred solution of compound **5aa** (99.1 mg, 0.20 mmol) in 2 ml of dry THF, NaBH₄ (30.3 mg, 0.80 mmol) was added. The resulting solution was stirred at room temperature for 10 h (TLC control, CH₂Cl₂–hexane, 2:1), then it was quenched with 5 ml of H₂O and neutralized with 1M HCl. Organic phase was extracted with EtOAc, dried over Na₂SO₄ and evaporated under reduced pressure to complete dryness. Residue was subjected to column chromatography (EtOAc–hexane, 1:3) to obtain reduction products **9** and **10** as white powders after recrystallisation from hexane.



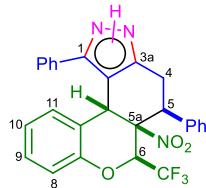
*(6*S**,6*a**R**,7*S**,10*a**R**)-10-((*E*)-Benzylidene)-6*a*-nitro-7-phenyl-6-(trifluoromethyl)-6,6*a*,7,8,10,10*a*-hexahydro-9*H*-benzo[*c*]chromen-9-one (**9**)*. Yield 21 mg (22%), white powder, mp 218–219 °C. IR (ATR): 1698, 1584, 1548, 1484, 1454, 1377, 1263, 1213 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.73 (dd, *J* = 17.4, 4.6 Hz, 1H), 2.97 (dd, *J* = 17.4, 14.4 Hz, 1H), 3.92 (dd, *J* = 14.4, 4.6 Hz, 1H), 5.04 (q, ³J_{H,F} = 7.1 Hz, 1H), 5.38 (s, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.21–7.25 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.39–7.45 (m, 6H), 7.51–7.56 (m, 2H), 7.93 (s, 1H); ¹⁹F NMR (471 MHz, CDCl₃) δ 92.09 (d, *J* = 7.1 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 39.5, 41.0, 42.8, 73.8 (q, ²J_{C,F} = 30.9 Hz, C-6), 86.4, 117.3, 118.8, 123.5, 123.5 (q, ¹J_{C,F} = 288.0 Hz, CF₃), 128.9 (2C), 129.2 (2C), 129.3 (2C), 129.4, 129.6, 129.7 (2C), 130.1, 130.4, 133.5, 134.1, 134.3, 140.2, 150.2, 196.6. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₁F₃NO₄ 480.1423, found 480.1411.



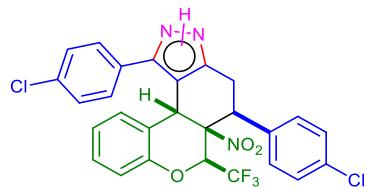
*((6*S**,6*a**R**,7*S**,9*S**,10*a**S**)-9-Hydroxy-6*a*-nitro-7-phenyl-6-(trifluoromethyl)-6*a*,7,8,9,10,10*a*-hexahydro-6*H*-benzo[*c*]chromen-10-yl)(phenyl)methanone (**10**)*. Yield 38 mg (38%), white powder, mp 167–168 °C. IR (ATR): 3548, 1670, 1582, 1553, 1489, 1452, 1379, 1273, 1218 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.17 (td, *J* = 13.7, 11.1 Hz, 1H, H^a-8), 2.27 (dt, *J* = 13.7, 3.2 Hz, 1H, H^b-8), 3.56 (dd, *J* = 13.7, 3.2 Hz, 1H, H-7), 3.69 (s, 1H, OH), 4.31 (td, *J* = 10.5, 3.2 Hz, 1H, H-9), 4.69 (dd, *J* = 10.0, 3.7 Hz, 1H, H-10), 4.79 (d, *J* = 3.7 Hz, 1H, H-10a), 5.01 (q, ³J_{H,F} = 7.2 Hz, 1H, H-6), 6.97 (t, *J* = 7.7 Hz, 1H, H-2), 7.08 (d, *J* = 7.8 Hz, 1H, H-4), 7.22–7.27 (m, 2H, H-1,3), 7.29–7.34 (m, 2H, H_o Ph), 7.39–7.44 (m, 3H, H_m, H_p Ph), 7.59 (t, *J* = 7.6 Hz, 2H, H_m Bz), 7.66 (t, *J* = 7.6 Hz, 1H, H_p Bz), 8.29 (d, *J* = 7.6 Hz, 2H, H_o Bz); ¹⁹F NMR (471 MHz, CDCl₃) δ 91.72 (d, *J* = 7.3 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 34.9, 39.6, 43.8, 53.1, 65.4, 74.1 (q, ²J_{C,F} = 31.0 Hz, C-6), 87.7, 117.9, 119.7, 123.3 (q, ¹J_{C,F} = 288.1 Hz, CF₃), 123.4, 127.4, 128.7 (2C), 128.7 (2C), 128.8, 129.5 (2C), 129.5 (2C), 129.7, 134.3, 136.2, 136.8, 150.1, 205.8. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₇H₂₃F₃NO₅ 498.1528, found 498.1516.

General procedure for the synthesis of pyrazoles **11.** To a stirred solution of hexahydro-9*H*-benzo[*c*]chromen-9-one **5** (0.10 mmol) in 1 ml of glacial acetic acid, a solution of hydrazine hydrate (1.0 mmol) in 0.5 mL of AcOH was added. Then, the mixture was stirred at reflux for 4 h (TLC control

CH_2Cl_2 -hexane (2:1)). After completion of the reaction, it was cooled down and poured into vigorously stirred water. The formed precipitate was filtered off, washed with water, dried, and then recrystallized from MeOH with addition of NaHCO_3 . Precipitate was again washed with water and dried under reduced pressure to obtain products **11**.

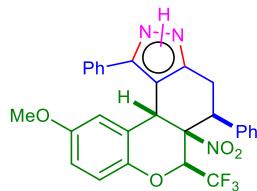


*(5*S**,5*a**R**,6*S**,11*b**S**)-5*a*-Nitro-1,5-diphenyl-6-(trifluoromethyl)-2(3),4,5,5*a*,6,11*b*-hexahydrochromeno[4,3-*e*]indazole (**11a**)*. Obtained according to the general procedure from **5aa** (49.5 mg). Yield 40.1 mg (75%), white powder, mp 162–163 °C. IR (ATR): 3401, 1585, 1552, 1487, 1454, 1373, 1354, 1270, 1211 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.02 (dd, $J = 16.9, 5.2$ Hz, 1H), 3.21 (dd, $J = 16.9, 13.2$ Hz, 1H), 3.74 (dd, $J = 13.2, 5.2$ Hz, 1H), 4.88 (q, $^3J_{\text{H},\text{F}} = 7.3$ Hz, 1H), 5.39 (s, 1H), 6.80 (t, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 8.2$ Hz, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.39–7.47 (m, 6H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.77 (d, $J = 7.6$ Hz, 2H), 10.30 (br. s, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ 90.97 (d, $J = 7.3$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 25.8, 34.8 (br. s, C-5*a*), 43.9, 74.0 (q, $^2J_{\text{C},\text{F}} = 30.9$ Hz, C-6), 86.7, 96.3, 112.6, 116.7, 122.3, 123.0, 123.5 (q, $^1J_{\text{C},\text{F}} = 285.5$ Hz, CF_3), 127.1 (2C), 127.8, 128.6 (2C), 129.0, 129.1, 129.2, 129.8 (2C), 129.9, 130.5 (2C), 131.5, 135.6, 148.9. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{F}_3\text{N}_3\text{O}_3$ 492.1530, found 492.1531.

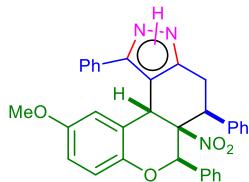


*(5*S**,5*a**R**,6*S**,11*b**S**)-1,5-Bis(4-chlorophenyl)-5*a*-nitro-6-(trifluoromethyl)-2(3),4,5,5*a*,6,11*b*-hexahydrochromeno[4,3-*e*]indazole (**11b**)*. Obtained according to the general procedure from **5am** (56.4 mg). Yield 51.7 mg (92%), white powder, mp 314–315 °C. IR (ATR): 3412, 1585, 1549, 1487, 1454, 1370, 1354, 1280, 1267, 1210 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.96 (dd, $J = 16.9, 5.2$ Hz, 1H), 3.13 (dd, $J = 16.9, 13.1$ Hz, 1H), 3.71 (dd, $J = 13.1, 5.2$ Hz, 1H), 4.82 (q, $^3J_{\text{H},\text{F}} = 7.2$ Hz, 1H), 5.33 (s, 1H), 6.83 (t, $J = 7.9$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 8.1$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 10.58 (br. s, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ 90.86 (d, $J = 7.2$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 25.5, 34.7 (br. s, C-5*a*), 43.2, 73.9 (d, $^2J_{\text{C},\text{F}} = 31.1$ Hz, C-6), 86.5, 112.7, 116.9, 122.0, 123.2, 123.3 (q, $^1J_{\text{C},\text{F}} = 287.6$ Hz, CF_3), 128.5 (2C), 128.9 (2C), 129.2, 129.5, 129.6, 130.0 (3C), 130.2, 131.7 (2C), 133.8,

135.2, 135.3, 148.7. HRMS (ESI) m/z : [M + H]⁺ calcd for C₂₇H₁₉Cl₂F₃N₃O₃ 560.0756, found 560.0738.



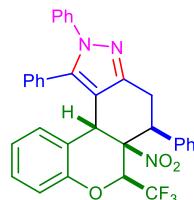
(5S,5aR*,6S*,11bS*)-10-Methoxy-5a-nitro-1,5-diphenyl-6-(trifluoromethyl)-2(3),4,5,5a,6,11b-hexahydrochromeno[4,3-*e*]indazole (11c).* Obtained according to the general procedure from **5ia** (52.5 mg). Yield 44.1 mg (86%), white powder, mp 169–170 °C. IR (ATR): 3065, 1552, 1494, 1454, 1355, 1271, 1201 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.02 (dd, *J* = 16.9, 5.1 Hz, 1H), 3.21 (dd, *J* = 16.9, 13.3 Hz, 1H), 3.26 (s, 3H), 3.76 (dd, *J* = 13.3, 5.1 Hz, 1H), 4.83 (q, ³J_{H,F} = 7.4 Hz, 1H), 5.42 (s, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 6.73 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 7.39–7.47 (m, 6H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H) (NH signal was not observed); ¹⁹F NMR (471 MHz, CDCl₃) δ 91.17 (d, *J* = 7.4 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 25.6, 35.0 (br. s, C-5a), 44.1, 55.4, 74.0 (q, ¹J_{C,F} = 31.1 Hz, C-6), 86.9, 112.7, 112.8, 116.7, 117.7, 122.6, 123.5 (q, ¹J_{C,F} = 287.9 Hz, CF₃), 127.4 (2C), 128.6 (2C), 129.0, 129.1, 129.8 (2C), 130.5 (2C), 132.0, 135.7, 142.4, 155.1 (2C were not observed). HRMS (ESI) m/z : [M + H]⁺ calcd for C₂₈H₂₃F₃N₃O₄ 522.1641, found 522.1619.



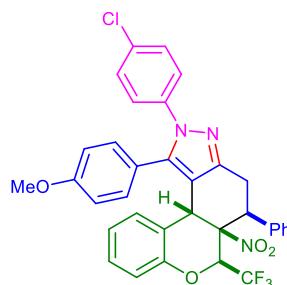
(5S,5aR*,6R*,11bS*)-10-Methoxy-5a-nitro-1,5,6-triphenyl-2(3),4,5,5a,6,11b-hexahydrochromeno[4,3-*e*]indazole (11d).* Obtained according to the general procedure from **5ma** (53.9 mg). Yield 39.7 mg (75%), white powder, mp 266–267 °C. IR (ATR): 3415, 1605, 1536, 1492, 1454, 1359, 1276, 1210 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.05 (dd, *J* = 16.7, 4.6 Hz, 1H), 3.31 (dd, *J* = 16.7, 13.2 Hz, 1H), 3.34 (s, 3H), 3.79 (dd, *J* = 13.2, 4.6 Hz, 1H), 5.19 (s, 1H), 5.38 (s, 1H), 6.45 (s, 1H), 6.79 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.95–7.03 (m, 3H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.36–7.48 (m, 6H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 10.18 (br. s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 26.0, 34.2, 44.1, 55.4, 78.4, 92.5, 112.9, 113.0, 116.6, 117.4, 123.1, 127.0 (2C), 127.1, 127.2 (2C), 128.3 (2C), 128.4, 128.7 (2C), 128.8, 129.3, 129.5 (2C), 130.8, 130.9, 136.2, 137.0, 144.8, 154.3 (2C were not observed). HRMS (ESI) m/z : [M + H]⁺ calcd for C₃₃H₂₈N₃O₄ 530.2074, found 530.2076.

General procedure for the synthesis of pyrazoles 12. A mixture of the corresponding arylhydrazine hydrochloride (0.40 mmol) and hexahydro-9*H*-benzo[*c*]chromen-9-one **5** (0.10 mmol) in the 1.5 mL of EtOH–AcOH (2:1) mixture was stirred under reflux for 12 h (TLC control). After completion of the

reaction, it was cooled down and poured into a vigorously stirred H₂O-saturated aqueous NaHCO₃ mixture, 2:1. The formed precipitate was filtered off, washed with water, dried, and then recrystallized from MeOH. Precipitate was again washed with water and dried under reduced pressure to obtain products **12**.

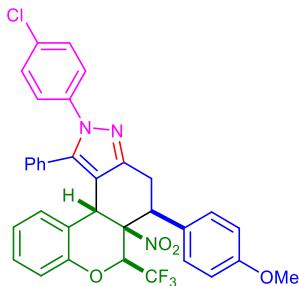


(5S*,5aR*,6S*,11bS*)-5a-Nitro-1,2,5-triphenyl-6-(trifluoromethyl)-2,4,5,5a,6,11b-hexahydrochromeno[4,3-e]indazole (12a). Obtained according to the general procedure from **5aa** (49.5 mg) and phenylhydrazine hydrochloride (57.8 mg). Yield 40.1 mg (71%), white powder, mp 270–271 °C. IR (ATR): 1598, 1587, 1549, 1486, 1454, 1366, 1354, 1276, 1221 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.15 (dd, *J* = 17.1, 5.2 Hz, 1H), 3.29 (dd, *J* = 17.1, 13.1 Hz, 1H), 3.80 (dd, *J* = 13.1, 5.2 Hz, 1H), 4.88 (q, ³J_{H,F} = 7.5 Hz, 1H), 5.26 (s, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.27–7.33 (m, 3H), 7.40–7.50 (m, 10H); ¹⁹F NMR (471 MHz, CDCl₃) δ 90.91 (d, *J* = 7.5 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 26.5, 34.5 (br, s, C-5a), 44.4, 74.0 (q, ²J_{C,F} = 30.8 Hz, C-6), 86.6, 115.3, 116.7, 122.4, 122.8, 123.4 (q, ¹J_{C,F} = 287.5 Hz, CF₃), 125.4 (2C), 127.5, 128.6 (2C), 128.9 (2C), 129.0, 129.1, 129.2, 129.6 (3C), 129.7 (2C), 130.5 (2C), 130.6, 135.9, 140.0, 141.1, 146.3, 148.9. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₃H₂₅F₃O₃ 568.1843, found 568.1852.

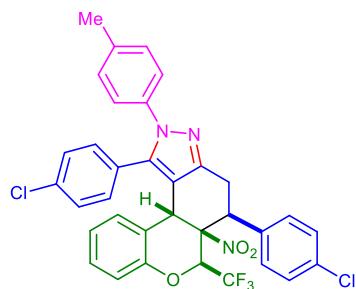


(5S*,5aR*,6S*,11bS*)-2-(4-Chlorophenyl)-1-(4-methoxyphenyl)-5a-nitro-5-phenyl-6-(trifluoromethyl)-2,4,5,5a,6,11b-hexahydrochromeno[4,3-e]indazole (12b). Obtained according to the general procedure from **5ac** (52.5 mg) and *p*-chlorophenylhydrazine hydrochloride (71.6 mg). Yield 47.9 mg (76%), white powder, mp 238–239 °C. IR (ATR): 1617, 1586, 1552, 1497, 1453, 1370, 1354, 1255, 1221 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.12 (dd, *J* = 17.1, 5.4 Hz, 1H), 3.26 (dd, *J* = 17.1, 13.1 Hz, 1H), 3.78 (dd, *J* = 13.1, 5.4 Hz, 1H), 3.85 (s, 3H), 4.87 (q, ³J_{H,F} = 7.3 Hz, 1H), 5.21 (s, 1H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.16–6.21 (m,

3H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.44 (s, 5H); ^{19}F NMR (471 MHz, CDCl_3) δ 90.91 (d, $J = 7.3$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 26.5, 34.5 (br. s, C-5a), 44.4, 55.4, 74.0 (q, $^2J_{\text{C},\text{F}} = 31.2$ Hz, C-6), 86.6, 115.3 (2C), 115.5, 116.7, 122.3, 122.4, 122.9, 123.4 (q, $^1J_{\text{C},\text{F}} = 287.4$ Hz, CF_3), 126.4 (2C), 128.6 (2C), 129.0, 129.1 (2C), 129.2, 129.6, 130.5 (2C), 130.9 (2C), 133.1, 135.8, 138.6, 141.1, 146.5, 148.9, 160.3. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{34}\text{H}_{26}\text{ClF}_3\text{N}_3\text{O}_4$ 632.1558, found 632.1556.

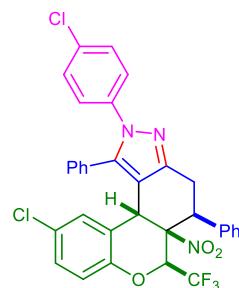


(5S*,5aR*,6S*,11bS*)-2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-5a-nitro-1-phenyl-6-(trifluoromethyl)-2,4,5,5a,6,11b-hexahydrochromeno[4,3-e]indazole (12c). Obtained according to the general procedure from **5ah** (52.5 mg) and *p*-chlorophenylhydrazine hydrochloride (71.6 mg). Yield 48.4 mg (77%), white powder, mp 218–219 °C. IR (ATR): 1610, 1585, 1552, 1494, 1454, 1371, 1260, 1216 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.11 (dd, $J = 17.2, 5.3$ Hz, 1H), 3.22 (dd, $J = 17.2, 13.2$ Hz, 1H), 3.75 (dd, $J = 13.2, 5.3$ Hz, 1H), 3.87 (s, 3H), 4.89 (q, $^3J_{\text{H},\text{F}} = 7.3$ Hz, 1H), 5.22 (s, 1H), 6.78 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.2$ Hz, 1H), 7.14–7.20 (m, 3H), 7.28 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.43–7.50 (m, 5H); ^{19}F NMR (471 MHz, CDCl_3) δ 90.89 (d, $J = 7.3$ Hz, CF_3); $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3) δ 26.7, 34.5 (br. s, C-5a), 43.8, 55.5, 74.1 (q, $^2J_{\text{C},\text{F}} = 30.8$ Hz, C-6), 86.7, 114.0 (2C), 115.8, 116.7, 122.4, 122.8, 123.5 (q, $^1J_{\text{C},\text{F}} = 287.2$ Hz, CF_3), 126.4 (2C), 127.6, 129.1 (2C), 129.2, 129.4, 129.5, 129.7 (2C), 129.8 (2C), 130.4, 131.5 (2C), 133.2, 138.6, 141.2, 146.8, 148.9, 160.1. HRMS (ESI) m/z : [M + H] $^+$ calcd for $\text{C}_{34}\text{H}_{26}\text{ClF}_3\text{N}_3\text{O}_4$ 632.1558, found 632.1549.

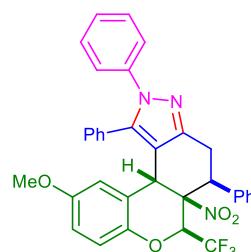


(5S*,5aR*,6S*,11bS*)-1,5-Bis(4-chlorophenyl)-5a-nitro-2-(p-tolyl)-6-(trifluoromethyl)-2,4,5,5a,6,11b-hexahydrochromeno[4,3-e]indazole (12d). Obtained according to the general procedure

from **5am** (56.4 mg) and *p*-methylphenylhydrazine hydrochloride (63.4 mg). Yield 41.5 mg (64%), white powder, mp 255–256 °C. IR (ATR): 1587, 1549, 1517, 1487, 1456, 1371, 1273, 1221 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H), 3.11 (dd, *J* = 17.1, 5.5 Hz, 1H), 3.22 (dd, *J* = 17.1, 13.1 Hz, 1H), 3.76 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.82 (q, ³*J*_{H,F} = 7.2 Hz, 1H), 5.20 (s, 1H), 6.77–6.86 (m, 2H), 7.04–7.16 (m, 5H), 7.17–7.23 (m, 1H), 7.34–7.47 (m, 8H); ¹⁹F NMR (471 MHz, CDCl₃) δ 90.80 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 21.2, 26.6, 34.5 (br. s), 43.9, 74.0 (q, ²*J*_{C,F} = 31.2 Hz), 86.5, 115.1, 116.8, 122.2, 123.0, 123.3 (q, ¹*J*_{C,F} = 287.3 Hz, CF₃), 125.3 (2C), 128.9 (2C), 129.1, 129.3, 129.4, 129.7 (2C), 130.0 (2C), 130.9 (2C), 131.9 (2C), 134.3, 135.1, 135.4, 137.3, 137.9, 139.9, 145.7, 148.8. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₄H₂₅Cl₂F₃N₃O₃ 650.1220, found 650.1234.

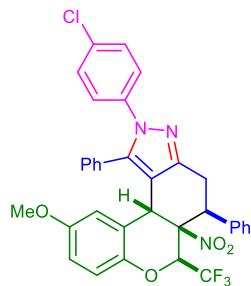


(*5S*,5aR*,6S*,11bS**)-10-Chloro-2-(4-chlorophenyl)-5*a*-nitro-1,5-diphenyl-6-(trifluoromethyl)-2,4,5,5*a*,6,11*b*-hexahydrochromeno[4,3-*e*]indazole (**12e**). Obtained according to the general procedure from **5ba** (53.0 mg) and *p*-chlorophenylhydrazine hydrochloride (71.6 mg). Yield 43.8 mg (69%), white powder, mp 234–235 °C. IR (ATR): 1586, 1547, 1504, 1494, 1479, 1369, 1277, 1216 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 3.16 (dd, *J* = 17.2, 5.4 Hz, 1H), 3.27 (dd, *J* = 17.2, 13.1 Hz, 1H), 3.72 (dd, *J* = 13.1, 5.4 Hz, 1H), 4.87 (q, ³*J*_{H,F} = 7.2 Hz, 1H), 5.18 (s, 1H), 6.87 (d, *J* = 1.6 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.38–7.54 (m, 10H); ¹⁹F NMR (471 MHz, CDCl₃) δ 91.05 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 26.5, 34.5 (q, ³*J*_{C,F} = 2.1 Hz, C-5a), 44.6, 74.1 (q, ²*J*_{C,F} = 31.2 Hz, C-6), 86.3, 115.2, 118.1, 123.3 (q, ¹*J*_{C,F} = 287.6 Hz, CF₃), 124.0, 126.4 (2C), 128.1, 128.7 (2C), 129.1 (2C), 129.2, 129.3, 129.65, 129.71 (3C), 130.0 (2C), 130.1, 130.4 (2C), 133.3, 135.5, 138.4, 141.2, 146.6, 147.5. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₃H₂₃Cl₂F₃N₃O₃ 636.1063, found 636.1060.

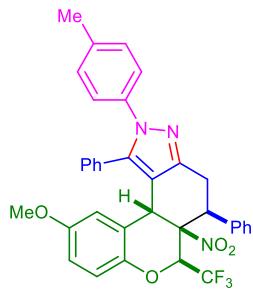


(*5S*,5aR*,6S*,11bS**)-10-Methoxy-5*a*-nitro-1,2,5-triphenyl-6-(trifluoromethyl)-2,4,5,5*a*,6,11*b*-hexahydrochromeno[4,3-*e*]indazole.

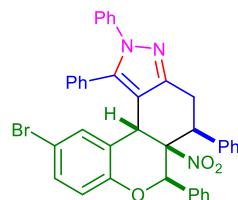
hexahydrochromeno[4,3-e]indazole (12f). Obtained according to the general procedure from **5ia** (52.5 mg) and phenylhydrazine hydrochloride (57.8 mg). Yield 42.9 mg (72%), white powder, mp 240–241 °C. IR (ATR): 1602, 1550, 1494, 1445, 1365, 1345, 1270, 1203 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 3.17 (dd, *J* = 17.1, 5.3 Hz, 1H), 3.29 (dd, *J* = 17.1, 13.3 Hz, 1H), 3.37 (s, 3H), 3.83 (dd, *J* = 13.3, 5.3 Hz, 1H), 4.83 (q, ³J_{H,F} = 7.3 Hz, 1H), 5.31 (s, 1H), 6.35 (d, *J* = 2.9 Hz, 1H), 6.73 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.27–7.34 (m, 3H), 7.39–7.52 (m, 10H); ¹⁹F NMR (471 MHz, CDCl₃) δ 90.99 (d, *J* = 7.3 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 26.5, 34.8 (br. s, C-5a), 44.6, 55.9, 74.0 (q, ²J_{C,F} = 30.9 Hz, C-6), 86.9, 113.0, 115.3, 116.4, 117.6, 122.8, 123.4 (q, ³J_{C,F} = 287.8 Hz, CF₃), 125.5 (2C), 127.6, 128.6 (2C), 128.98, 128.99 (2C), 129.3, 129.6 (2C), 129.7 (2C), 130.5 (2C), 130.6, 135.9, 139.9, 140.8, 142.5, 146.5, 155.1. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₄H₂₇F₃N₃O₄ 598.1954, found 598.1934.



*(5*S**,5*a**R**,6*S**,11*b**S**)-2-(4-Chlorophenyl)-10-methoxy-5*a*-nitro-1,5-diphenyl-6-(trifluoromethyl)-2,4,5,5*a*,6,11*b*-hexahydrochromeno[4,3-e]indazole (12g).* Obtained according to the general procedure from **5ia** (52.5 mg) and *p*-chlorophenylhydrazine hydrochloride (71.6 mg). Yield 45.4 mg (72%), white powder, mp 242–243 °C. IR (ATR): 1595, 1547, 1463, 1447, 1373, 1354, 1272, 1206 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 3.15 (dd, *J* = 17.1, 5.3 Hz, 1H), 3.28 (dd, *J* = 17.1, 13.3 Hz, 1H), 3.38 (s, 3H), 3.82 (dd, *J* = 13.3, 5.3 Hz, 1H), 4.82 (q, ³J_{H,F} = 7.2 Hz, 1H), 5.28 (s, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.41–7.51 (m, 10H); ¹⁹F NMR (471 MHz, CDCl₃) δ 91.00 (d, *J* = 7.2 Hz, 3F); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 26.5, 34.7 (br. s, C-5a), 44.5, 55.9, 74.0 (q, ²J_{C,F} = 30.9 Hz, C-6), 86.8, 113.0, 115.7, 116.3, 117.7, 122.6, 123.4 (q, ¹J_{C,F} = 287.8 Hz, CF₃), 126.5 (2C), 128.6 (2C), 129.0, 129.1 (2C), 129.5, 129.6 (2C), 129.9 (2C), 130.3, 130.5 (2C), 133.3, 135.8, 138.5, 140.8, 142.5, 146.9, 155.1. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₄H₂₆ClF₃N₃O₄ 632.1564, found 632.1572.



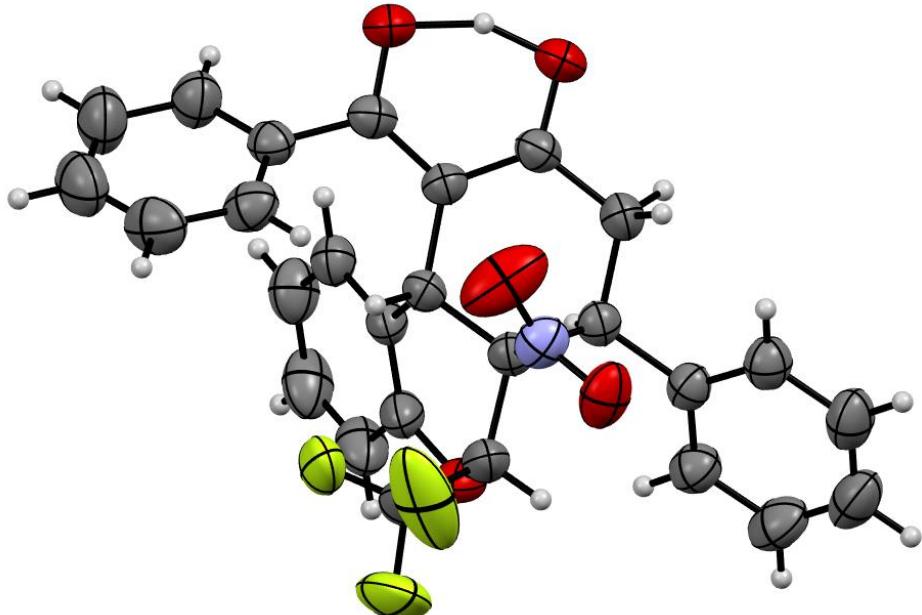
(5S,5aR*,6S*,11bS*)-10-Methoxy-5a-nitro-1,5-diphenyl-2-(*p*-tolyl)-6-(trifluoromethyl)-2,4,5,5a,6,11b-hexahydrochromeno[4,3-*e*]indazole (12h).* Obtained according to the general procedure from **5ia** (52.5 mg) and *p*-methylphenylhydrazine hydrochloride (63.4 mg). Yield 46.0 mg (75%), white powder, mp 220–221 °C. IR (ATR): 1613, 1548, 1517, 1496, 1464, 1448, 1374, 1354, 1269, 1205 cm^{−1}; ¹H NMR (600 MHz, CDCl₃) δ 2.35 (s, 3H), 3.16 (dd, *J* = 17.1, 4.9 Hz, 1H), 3.29 (dd, *J* = 17.1, 13.2 Hz, 1H), 3.36 (s, 3H), 3.83 (dd, *J* = 13.2, 4.9 Hz, 1H), 4.82 (q, ³J_{H,F} = 7.2 Hz, 1H), 5.30 (s, 1H), 6.35 (d, *J* = 1.5 Hz, 1H), 6.72 (dd, *J* = 8.9, 1.5 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 7.11 (s, 4H), 7.39–7.50 (m, 10H); ¹⁹F NMR (471 MHz, CDCl₃) δ 90.99 (d, *J* = 7.2 Hz, CF₃); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 21.2, 26.5, 34.8 (br. s, C-5a), 44.6, 55.9, 74.0 (q, ²J_{C,F} = 30.8 Hz, C-6), 86.9, 112.9, 115.0, 116.4, 117.6, 122.8, 123.4 (q, ¹J_{C,F} = 287.6 Hz, CF₃), 125.3 (2C), 128.6 (2C), 128.9, 129.1, 129.5 (2C), 129.6 (4C), 130.6 (2C), 130.7, 136.0, 137.5, 140.7, 142.5, 146.2, 155.1 (1C was not observed). HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₅H₂₉F₃N₃O₄ 612.2110, found 612.2098.



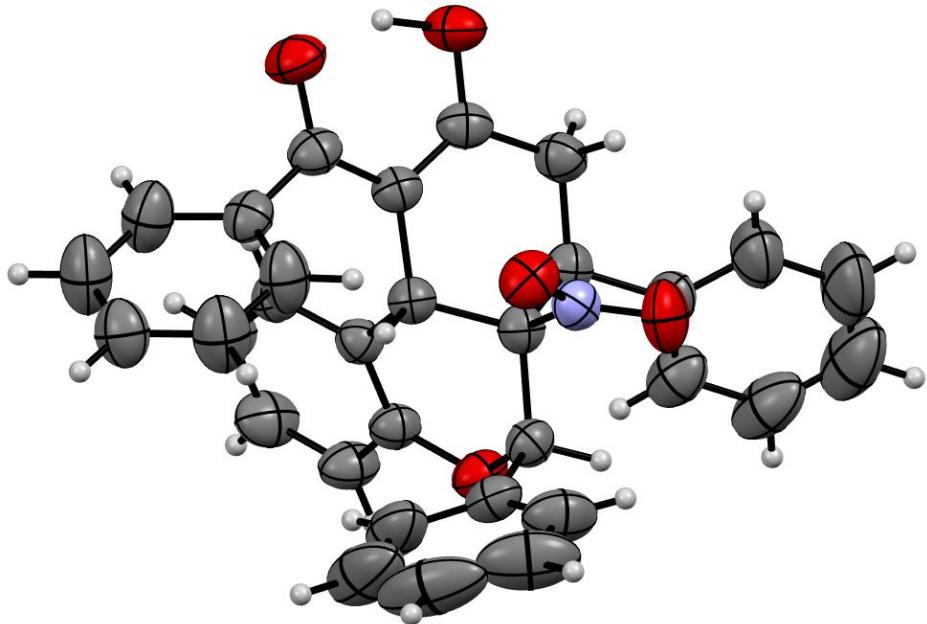
(5S,5aR*,6R*,11bS*)-10-Bromo-5a-nitro-1,2,5,6-tetraphenyl-2,4,5,5a,6,11b-hexahydrochromeno[4,3-*e*]indazole (12i).* Obtained according to the general procedure from **5la** (58.2 mg) and phenylhydrazine hydrochloride **10a** (57.8 mg). Yield 56.6 mg (86%), white powder, mp 318–319 °C. IR (ATR): 1600, 1542, 1508, 1496, 1475, 1368, 1273, 1225 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 3.20 (dd, *J* = 16.9, 5.1 Hz, 1H), 3.37 (dd, *J* = 16.9, 13.2 Hz, 1H), 3.75 (dd, *J* = 13.2, 5.1 Hz, 1H), 5.02 (s, 1H), 5.42 (s, 1H), 6.90–6.97 (m, 3H), 7.03 (s, 1H), 7.18–7.35 (m, 10H), 7.37–7.50 (m, 7H), 7.53–7.59 (m, 2H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 27.0, 33.5, 44.6, 78.6, 91.8, 113.9, 115.2, 118.2, 124.9, 125.2 (2C), 126.9 (2C), 127.4, 128.4 (2C), 128.5, 128.8 (2C), 128.9 (2C), 129.2, 129.5, 129.57 (2C), 129.63 (2C), 130.5, 130.8 (2C), 132.1, 132.6, 135.7, 137.0, 139.9, 141.3, 147.0, 150.3. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₈H₂₉BrN₃O₃ 654.1387, found 654.1383.

X-ray crystallography

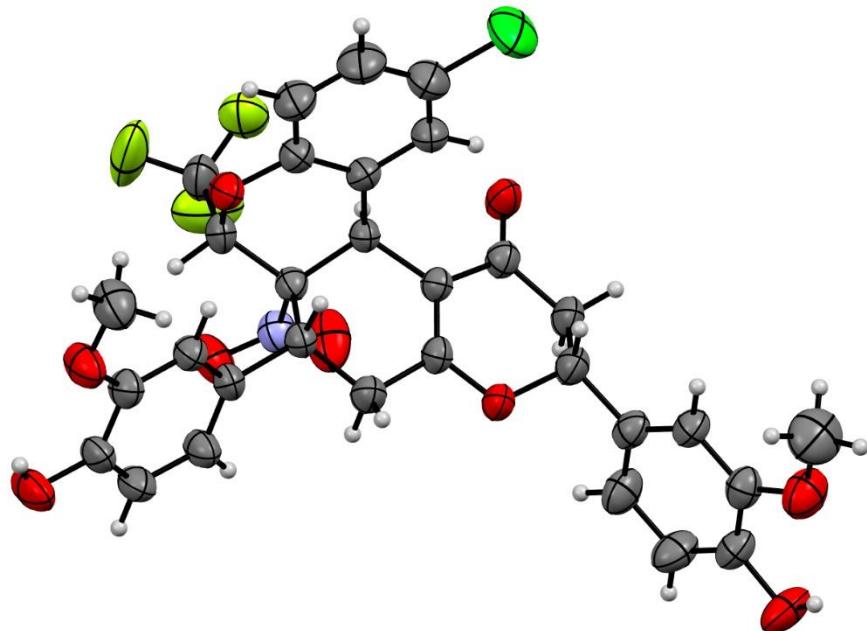
Crystals of **5aa**, **5ka**, **8a** and **12e** were grown by the slow evaporation of an acetonitrile solution, **7d** - of a toluene solution. Diffraction data were collected on a Xcalibur 3 automatic diffractometer using the standard procedure (Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromator, ω -scanning, 293(2) K). An empirical adjustment for absorption was introduced. The structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELX-97 program package.³ All non-hydrogen atoms were refined with anisotropic atomic displacement and hydrogen atoms were included at the calculated positions using a riding model. The geometrical parameters were analysed using the programs OLEX2.⁴



Crystal data for 5aa (C₂₇H₂₀F₃NO₅, 495.45). Triclinic crystals, space group P $\bar{1}$, $a = 9.7920(6)$, $b = 12.2767(8)$ and $c = 19.2845(12) \text{ \AA}$, $\beta = 85.247(5)^\circ$ $V = 2307.0(3) \text{ \AA}^3$, $D_c = 1.426$, absorption coefficient $\mu = 0.114 \text{ mm}^{-1}$, $Z = 4$. The intensities of 12399 independent reflections ($R_{\text{int}} = 0.0522$) were measured. The final discrepancy factors $R_1 = 0.0635$, $wR_2 = 0.1346$, GooF = 1.001 for 5586 reflections with $I > 2\sigma(I)$; $R_1 = 0.1528$, $wR_2 = 0.1968$ (all data). Largest different peaks and holes: 0.204 and -0.296 e \AA^{-3} . Completeness to $\Theta = 25.242^\circ$ (99.2%). Deposition number CCDC 2154343.

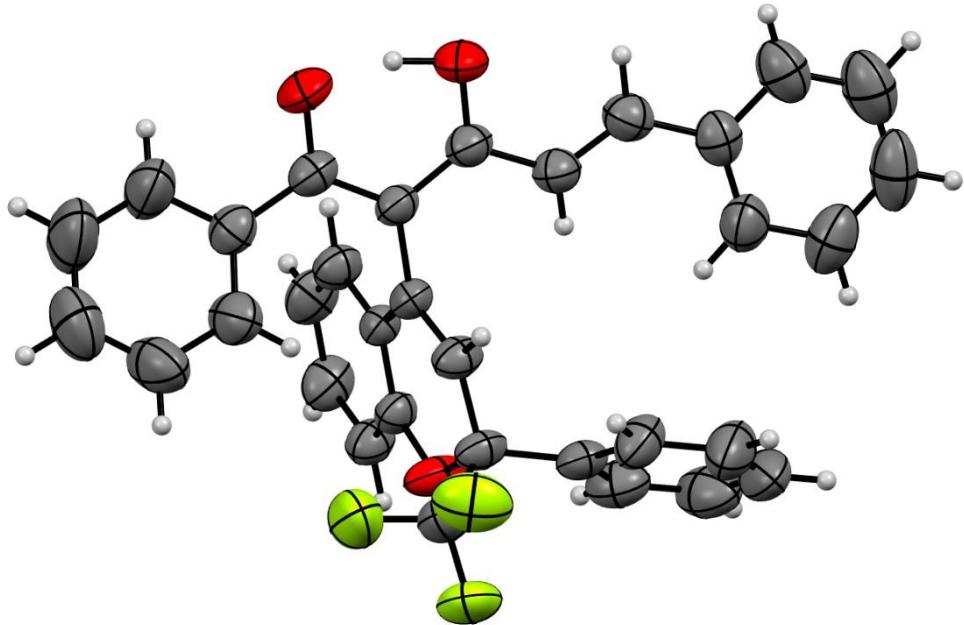


Crystal data for 5ka ($C_{32}H_{25}NO_5$, 503.53). Monoclinic crystals, space group $P2_1/c$, $a = 14.4214(10)$, $b = 12.2255(9)$ and $c = 14.5032(10)$ Å, $\beta = 95.431(7)^\circ$ $V = 2545.6(3)$ Å 3 , $D_c = 1.314$, absorption coefficient $\mu = 0.089$ mm $^{-1}$, $Z = 4$. The intensities of 6968 independent reflections ($R_{\text{int}} = 0.0448$) were measured. The final discrepancy factors $R_1 = 0.1294$, $wR_2 = 0.1544$, $\text{GooF} = 1.005$ for 3480 reflections with $I > 2\sigma(I)$; $R_1 = 0.1294$, $wR_2 = 0.2183$ (all data). Largest different peaks and holes: 0.26 and -0.25 e Å $^{-3}$. Completeness to $\Theta = 26.000^\circ$ (99.4%). Deposition number CCDC 2154342.

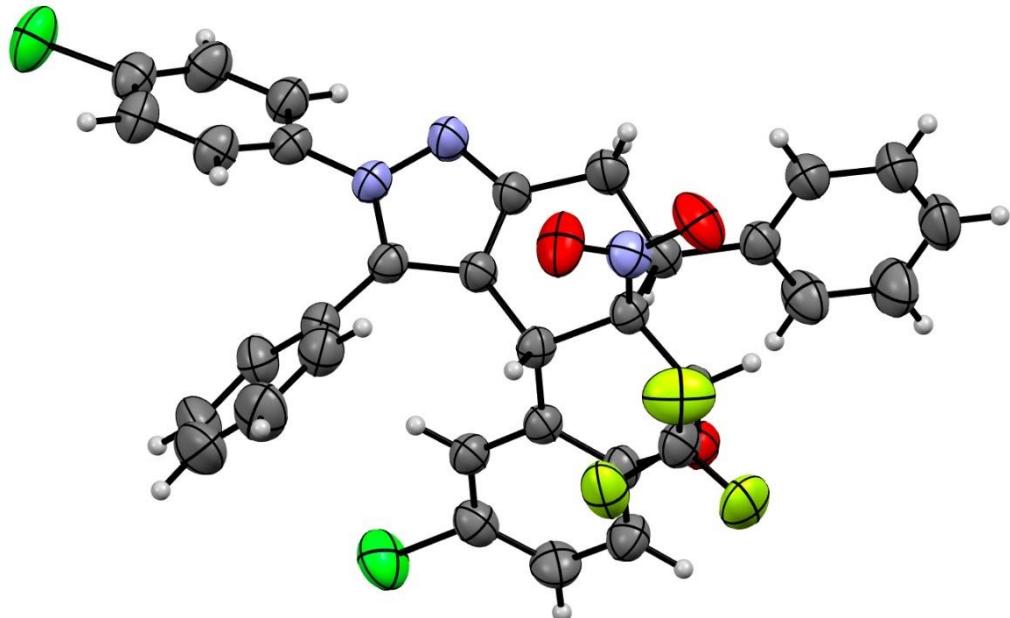


Crystal data for 7d ($C_{31}H_{25}ClF_3NO_9$, 647.98). Triclinic crystals, space group $P\bar{1}$, $a = 8.9834(10)$, $b = 11.4504(11)$ and $c = 19.4781(18)$ Å, $\beta = 86.642(8)^\circ$ $V = 1912.7(3)$ Å 3 , $D_c = 1.2850$, absorption coefficient $\mu = 0.168$ mm $^{-1}$, $Z = 2$. The intensities of 8637 independent reflections ($R_{\text{int}} = 0.0383$) were measured. The final discrepancy factors $R_1 = 0.073808$, $\text{GooF} = 1.043143$ for 3589 reflections with $I >$

$2\sigma(I)$; $R_1 = 0.177662$, $wR_2 = 0.225982$ (all data). Completeness to $\Theta = 26.000^\circ$ (98.79%). Deposition number CCDC 2154345.



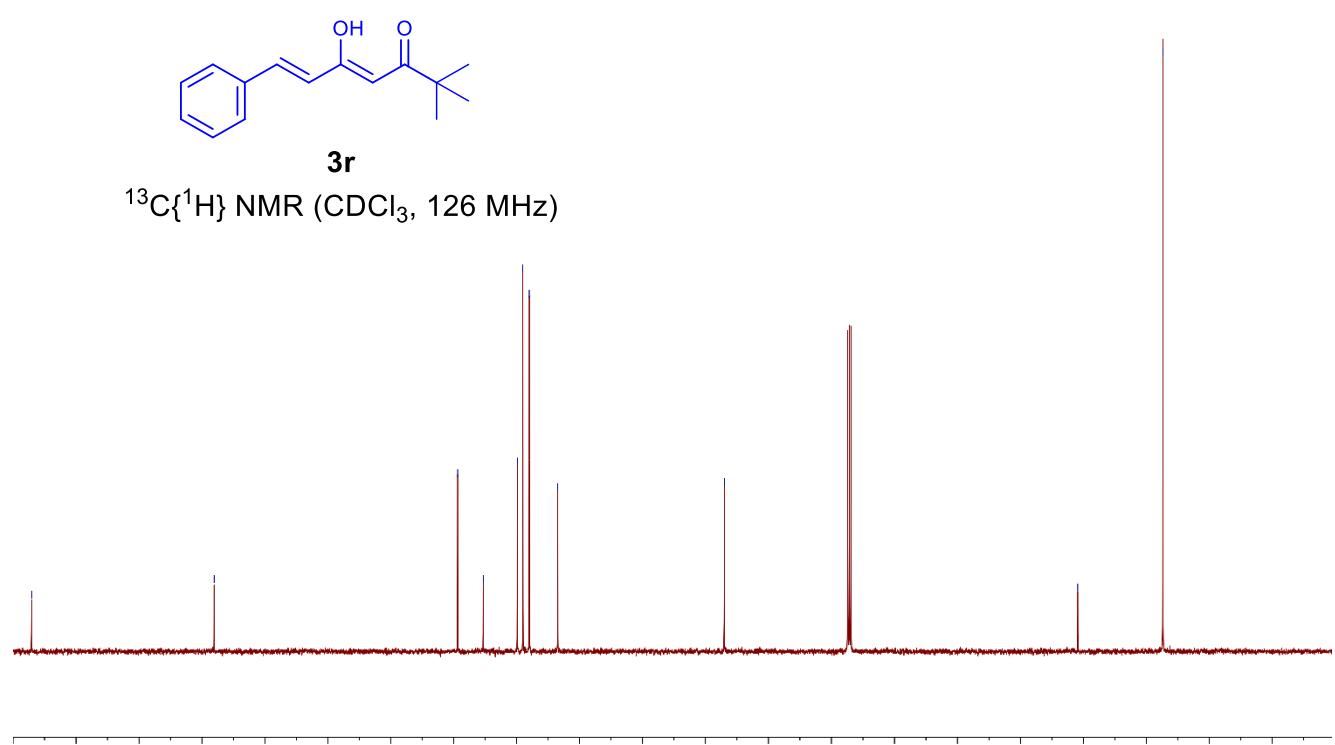
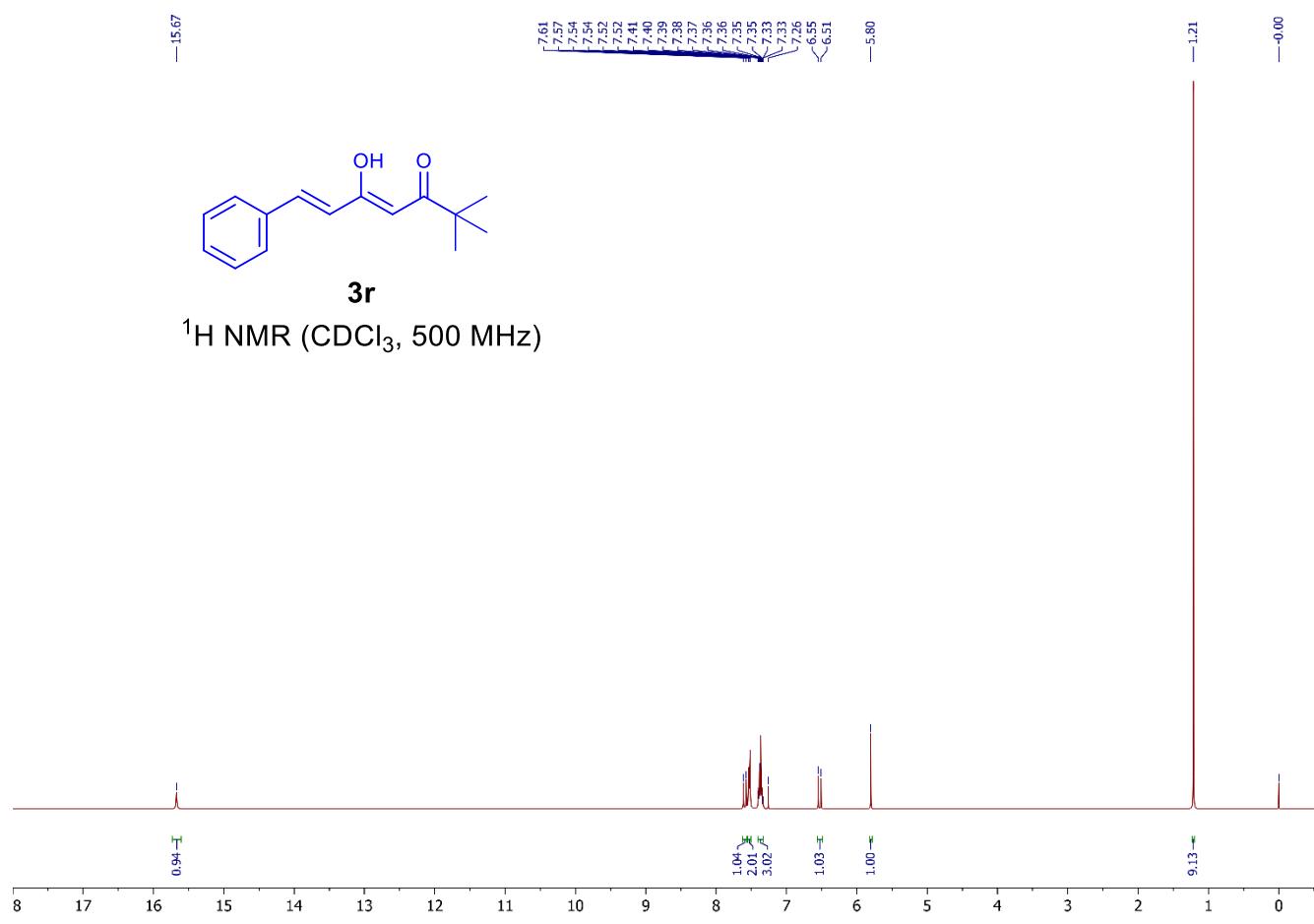
Crystal data for 8a ($C_{33}H_{23}F_3O_3$, 524.51). Triclinic crystals, space group $P\bar{1}$, $a = 11.9059(6)$, $b = 13.1467(9)$ and $c = 16.8474(12)$ Å, $\beta = 94.131(5)^\circ$ $V = 2593.6(3)$ Å 3 , $D_c = 1.343$, absorption coefficient $\mu = 0.100$ mm $^{-1}$, $Z = 4$. The intensities of 13600 independent reflections ($R_{\text{int}} = 0.0311$) were measured. The final discrepancy factors $R_1 = 0.0659$, $wR_2 = 0.1371$, $\text{GooF} = 1.028$ for 5830 reflections with $I > 2\sigma(I)$; $R_1 = 0.1758$, $wR_2 = 0.2033$ (all data). Completeness to $\Theta = 26.00^\circ$ (98.72%). Deposition number CCDC 2154344.

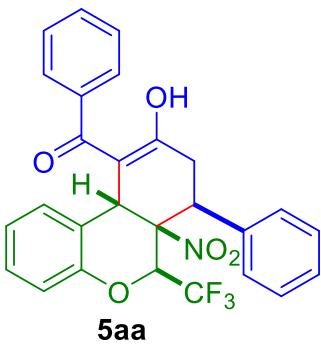


Crystal data for 12e ($\mathbf{C_{33}H_{22}Cl_2F_3N_3O_3$, 636.43). Triclinic crystals, space group $P\bar{1}$, $a = 8.4663(7)$, $b = 12.6932(12)$ and $c = 13.8600(13)$ Å, $\beta = 78.202(7)^\circ$ $V = 1433.3(2)$ Å³, $D_c = 1.475$, absorption coefficient $\mu = 0.287$ mm⁻¹, $Z = 2$. The intensities of 7704 independent reflections ($R_{\text{int}} = 0.0527$) were measured. The final discrepancy factors $R_1 = 0.0604$, $wR_2 = 0.1253$, $\text{GooF} = 1.020$ for 3497 reflections with $I > 2\sigma(I)$; $R_1 = 0.1474$, $wR_2 = 0.1880$ (all data). Largest different peaks and holes: 0.29 and -0.38 e Å⁻³. Completeness to $\Theta = 26.000^\circ$ (99.0%). Deposition number CCDC 2154346.

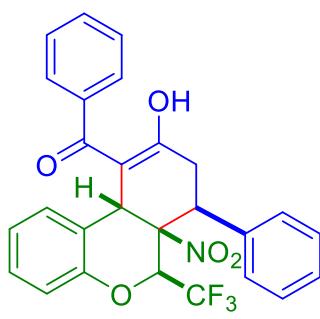
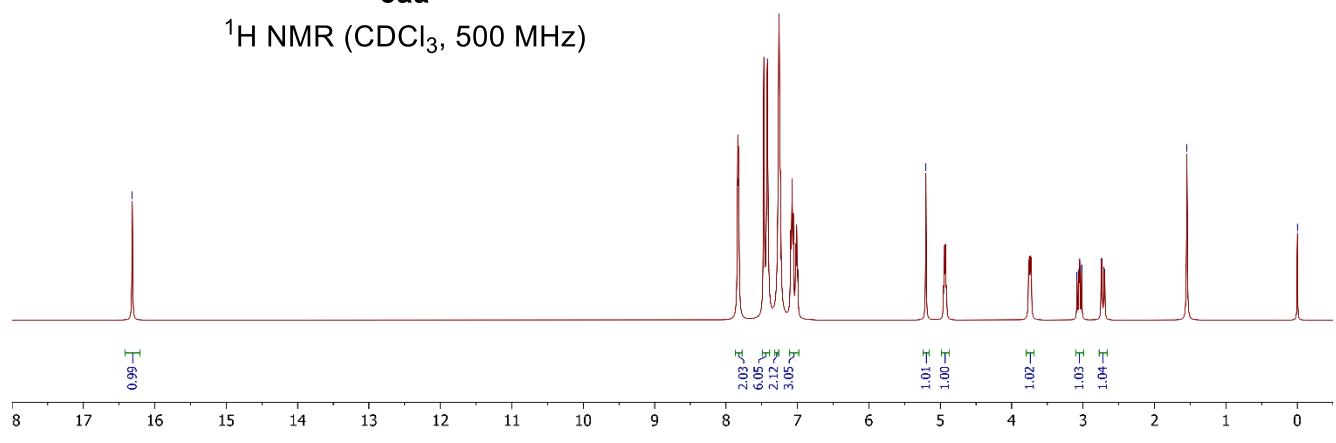
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1. (a) V. Y. Korotaev, I. B. Kutyashev, V. Y. Sosnovskikh, *Heteroat. Chem.*, 2005, 16, 492; (b) T. Sakakibara, M. Koezuka, R. Sudoh, *Bull. Chem. Soc. Jpn.*, 1978, 51, 3095; (c) A. Y. Barkov, V. Y. Korotaev, I. V. Kotovich, N. S. Zimnitskiy, I. B. Kutyashev, V. Y. Sosnovskikh, *Chem. Heterocycl. Compd.*, 2016, 52, 814.
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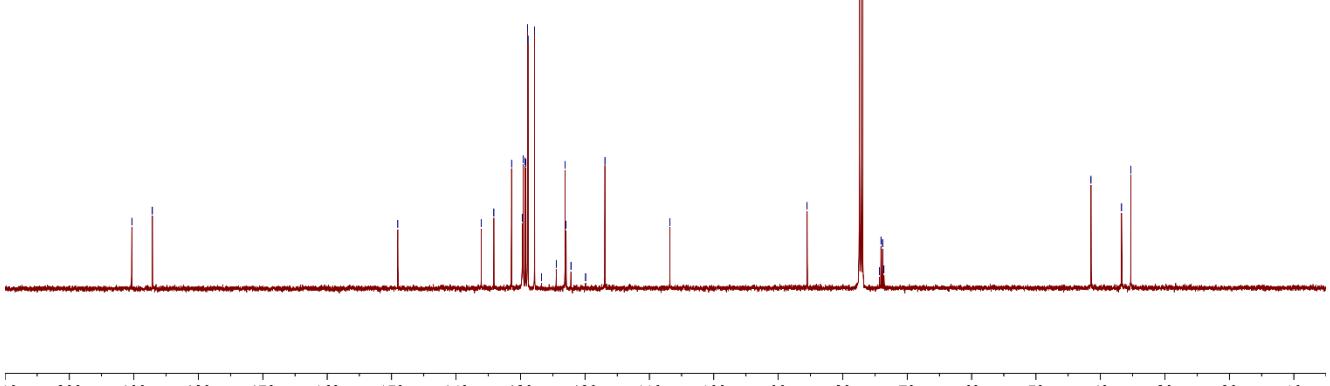


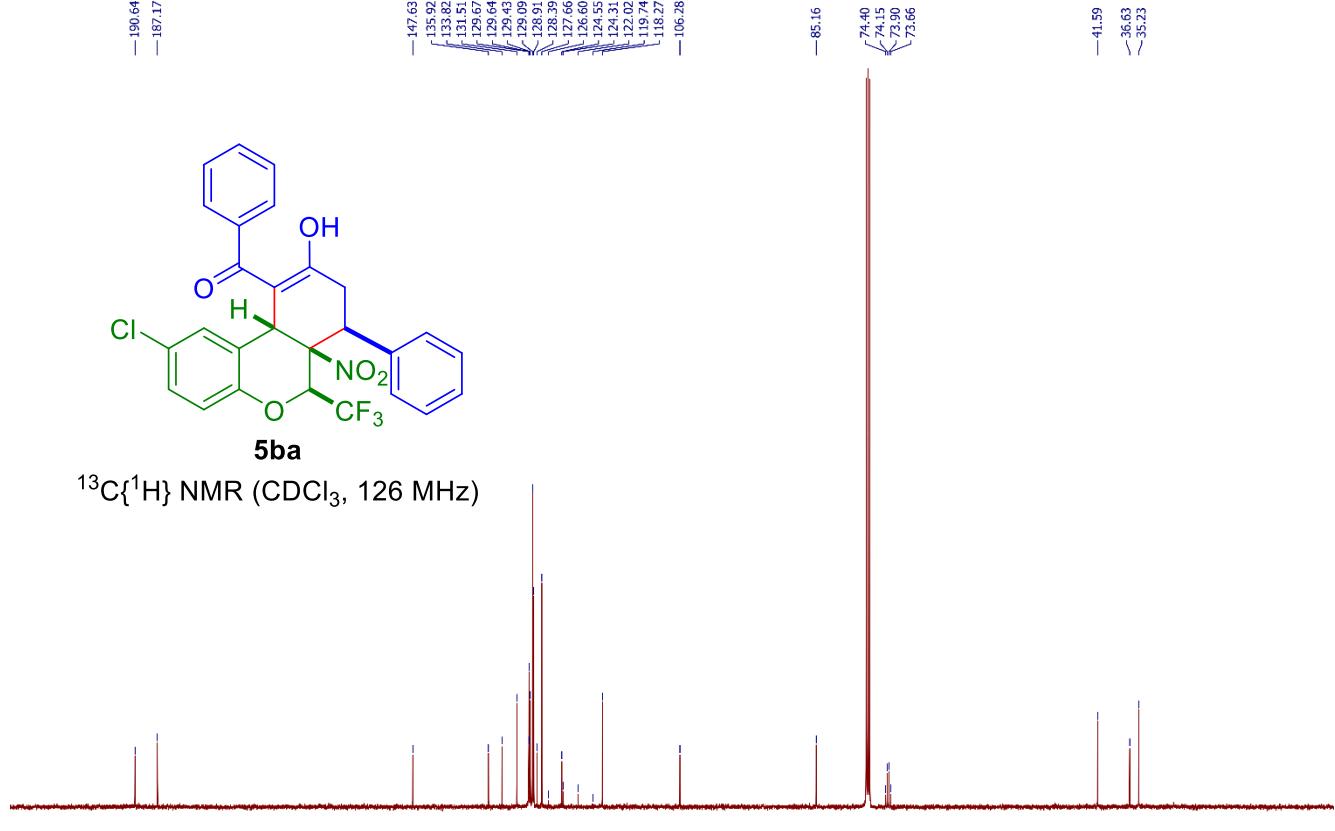
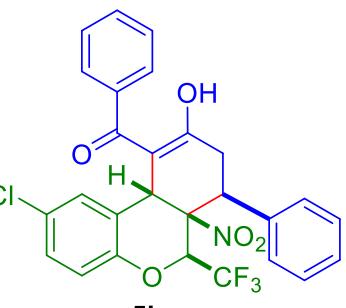
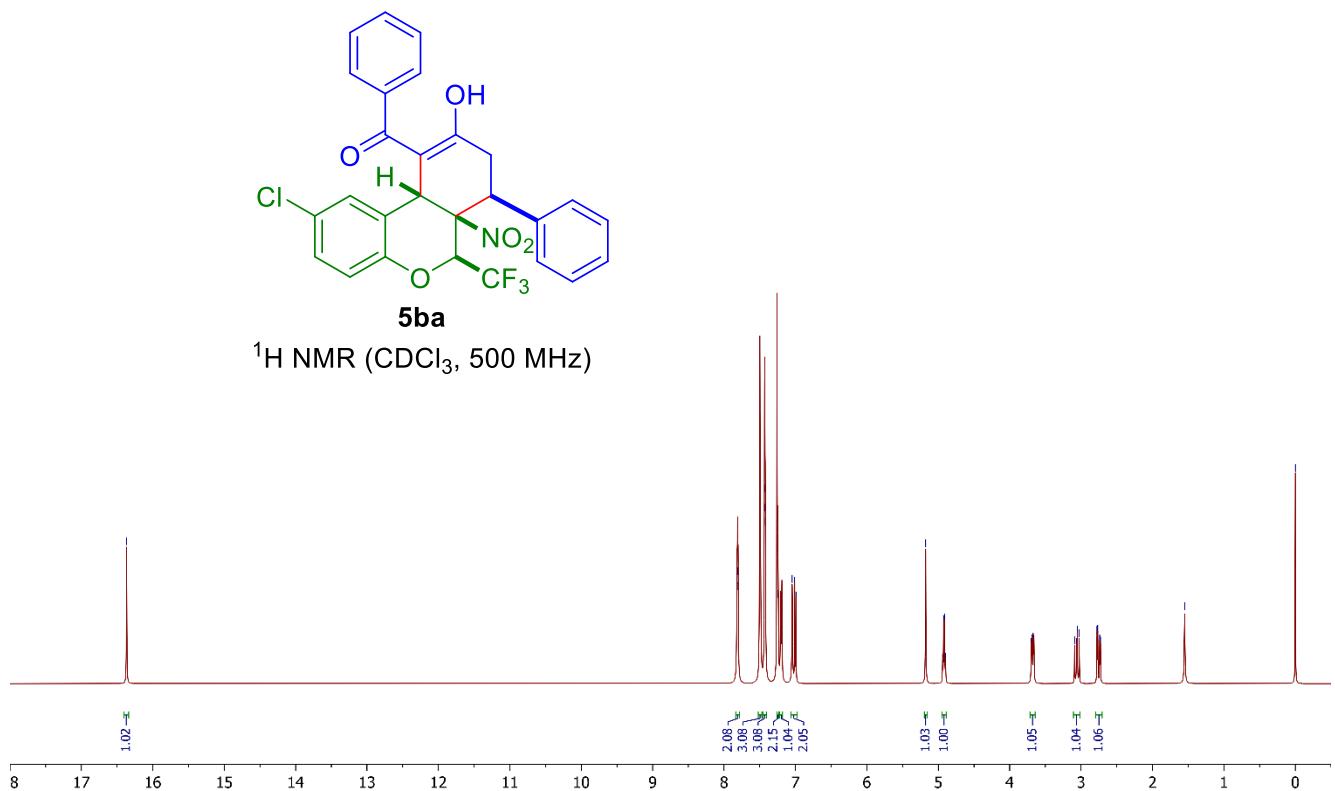


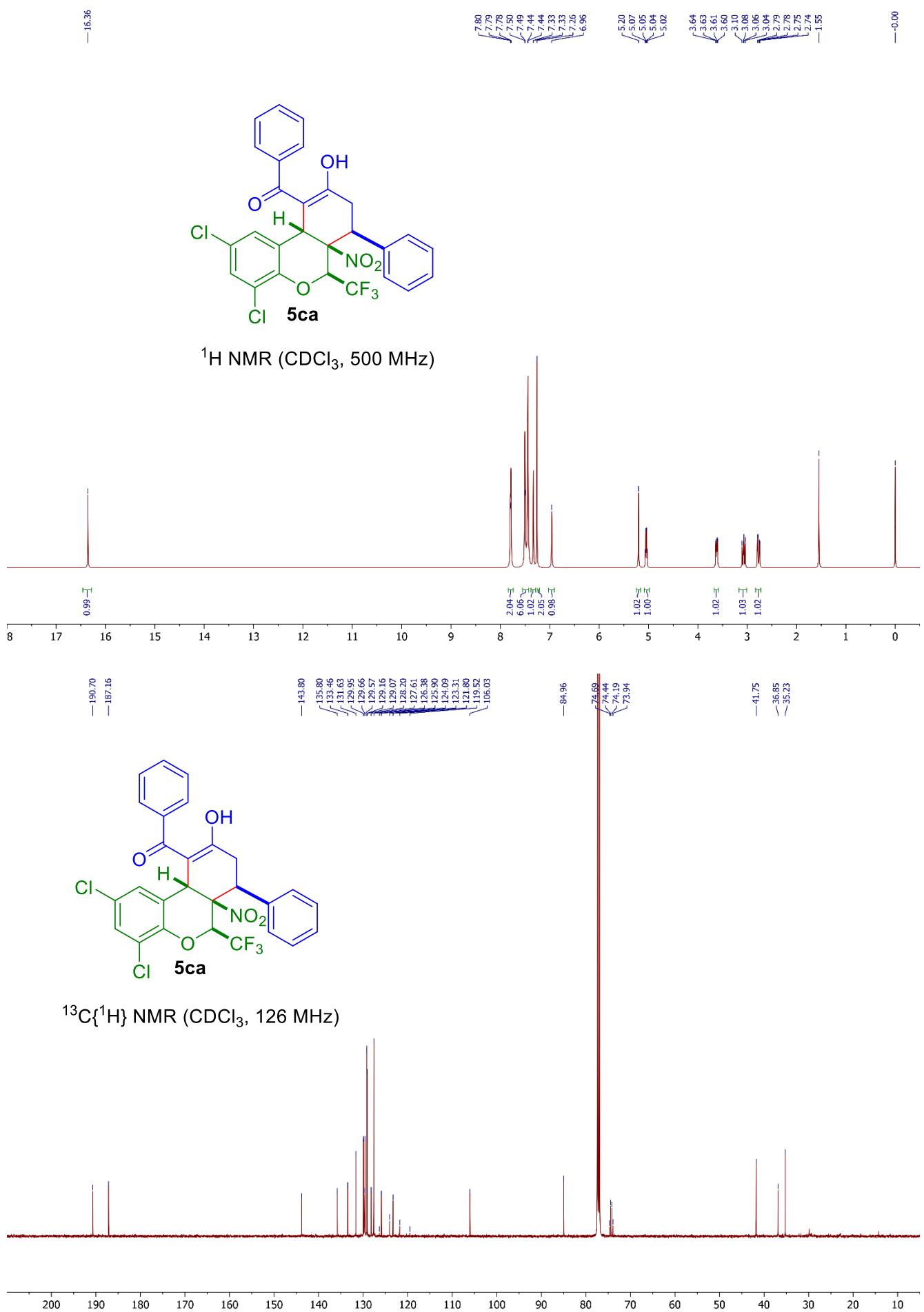
^1H NMR (CDCl_3 , 500 MHz)

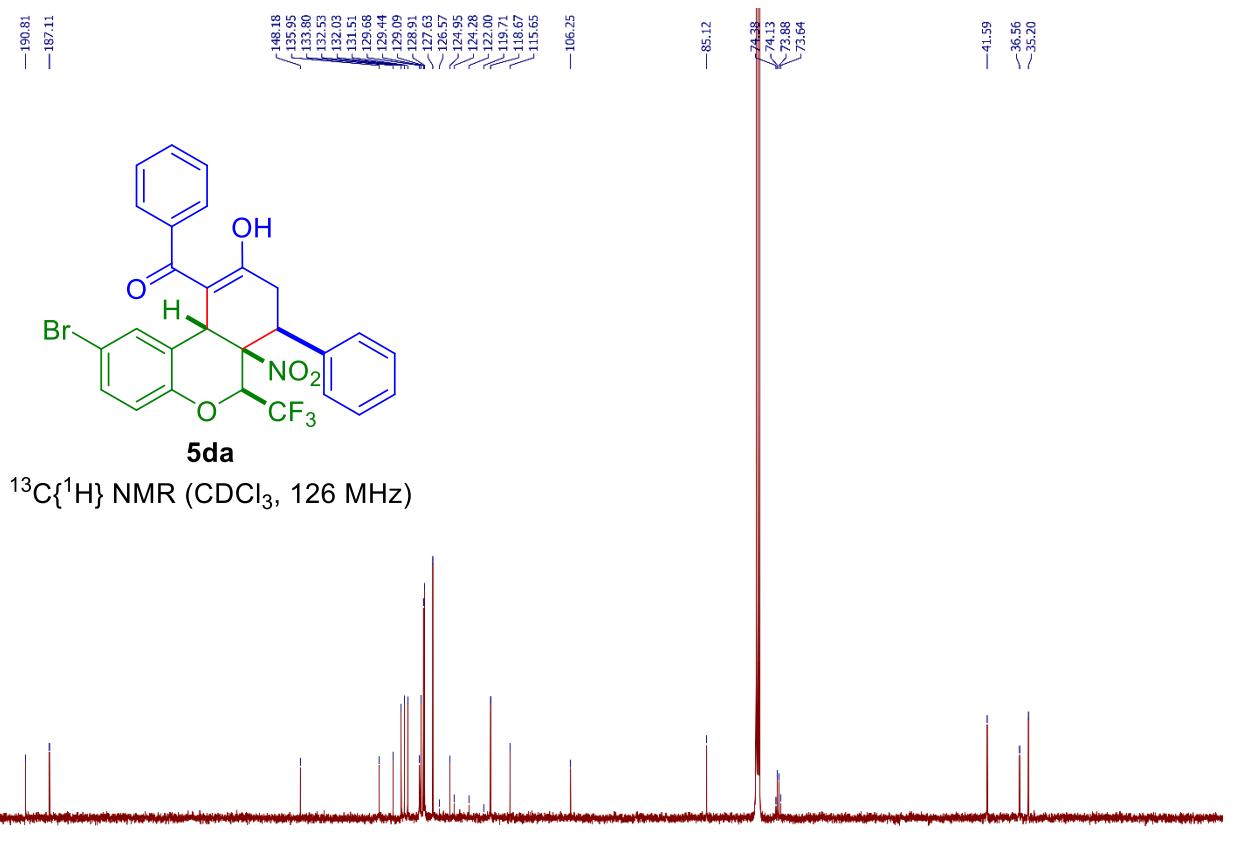
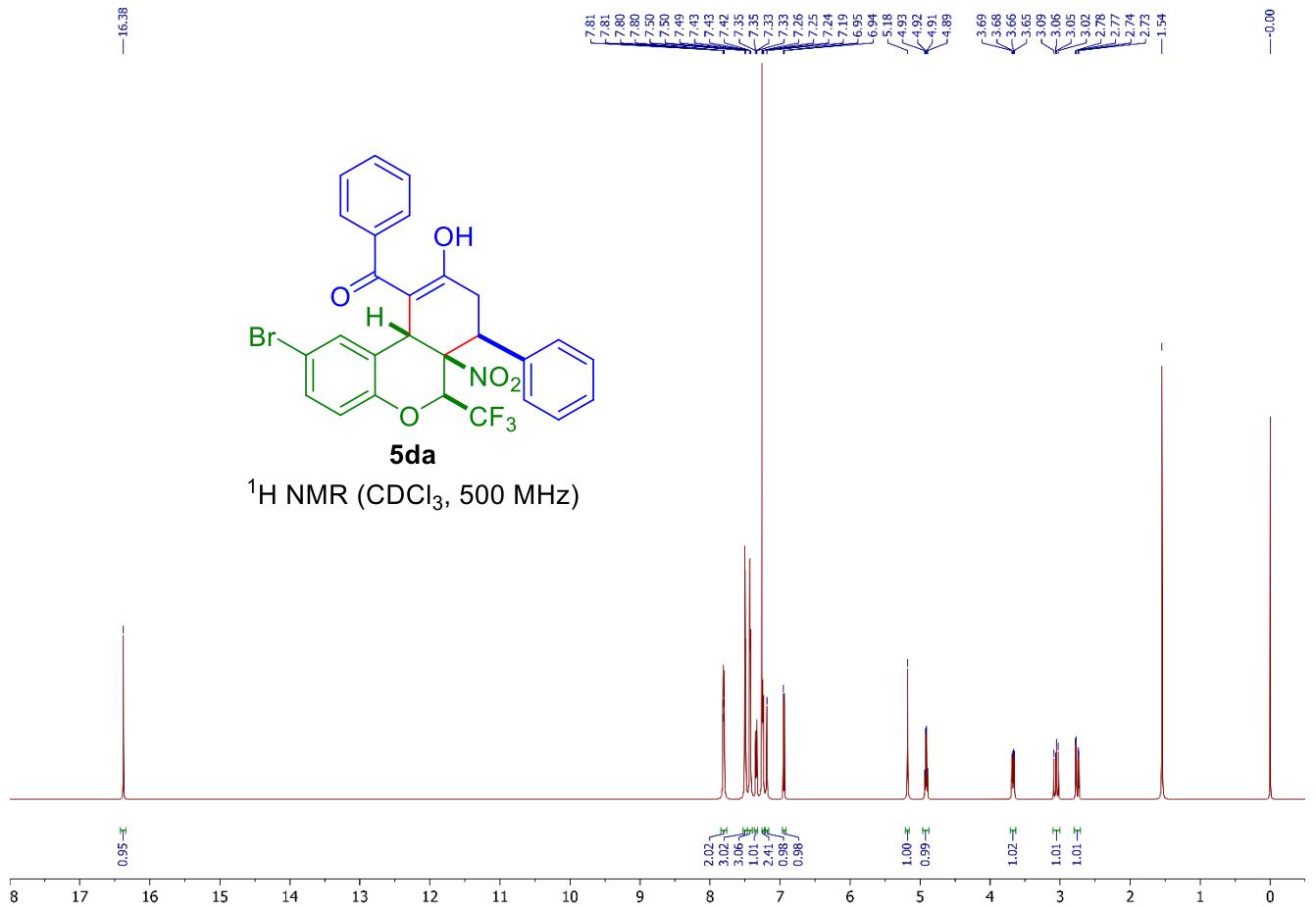


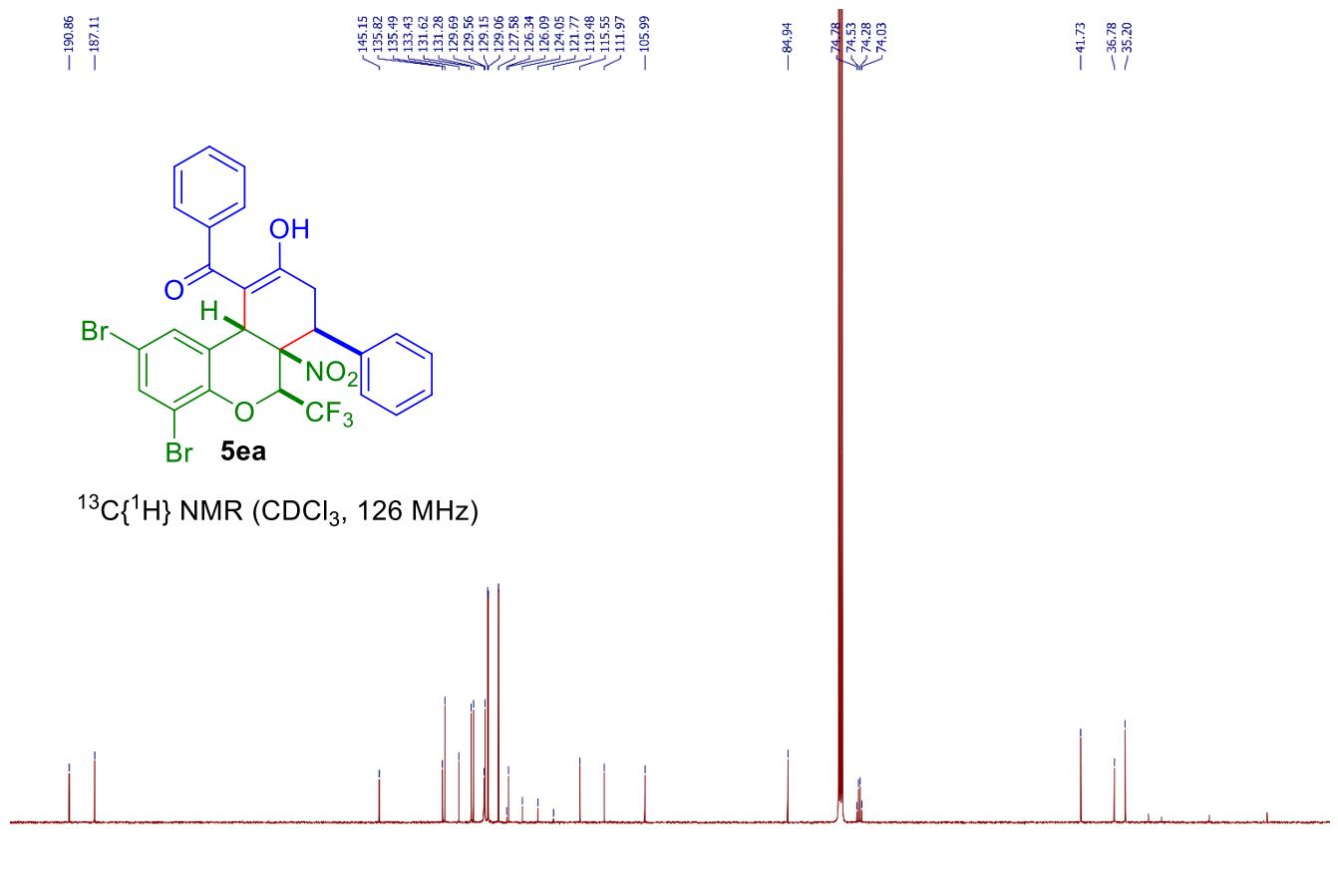
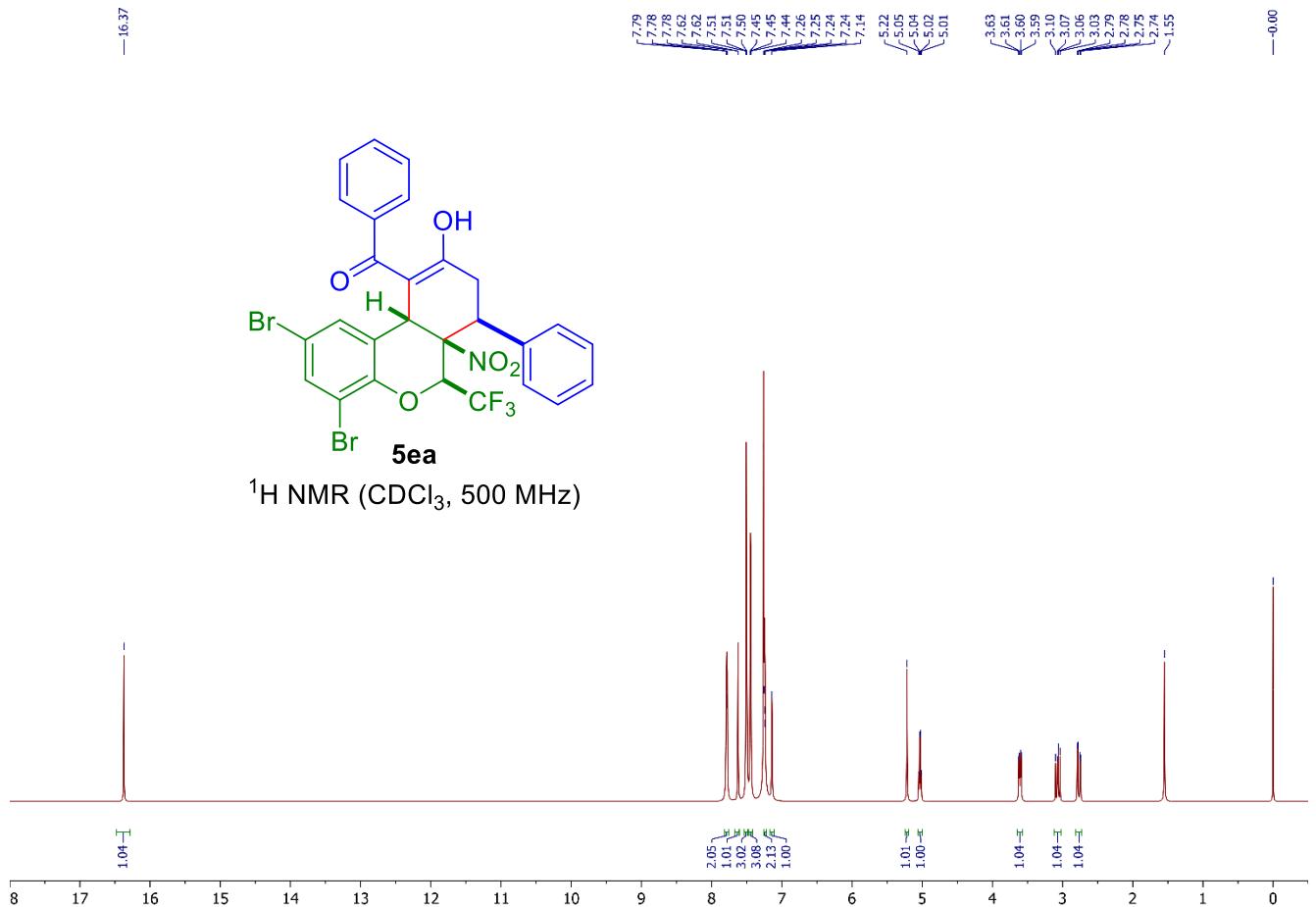
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz)

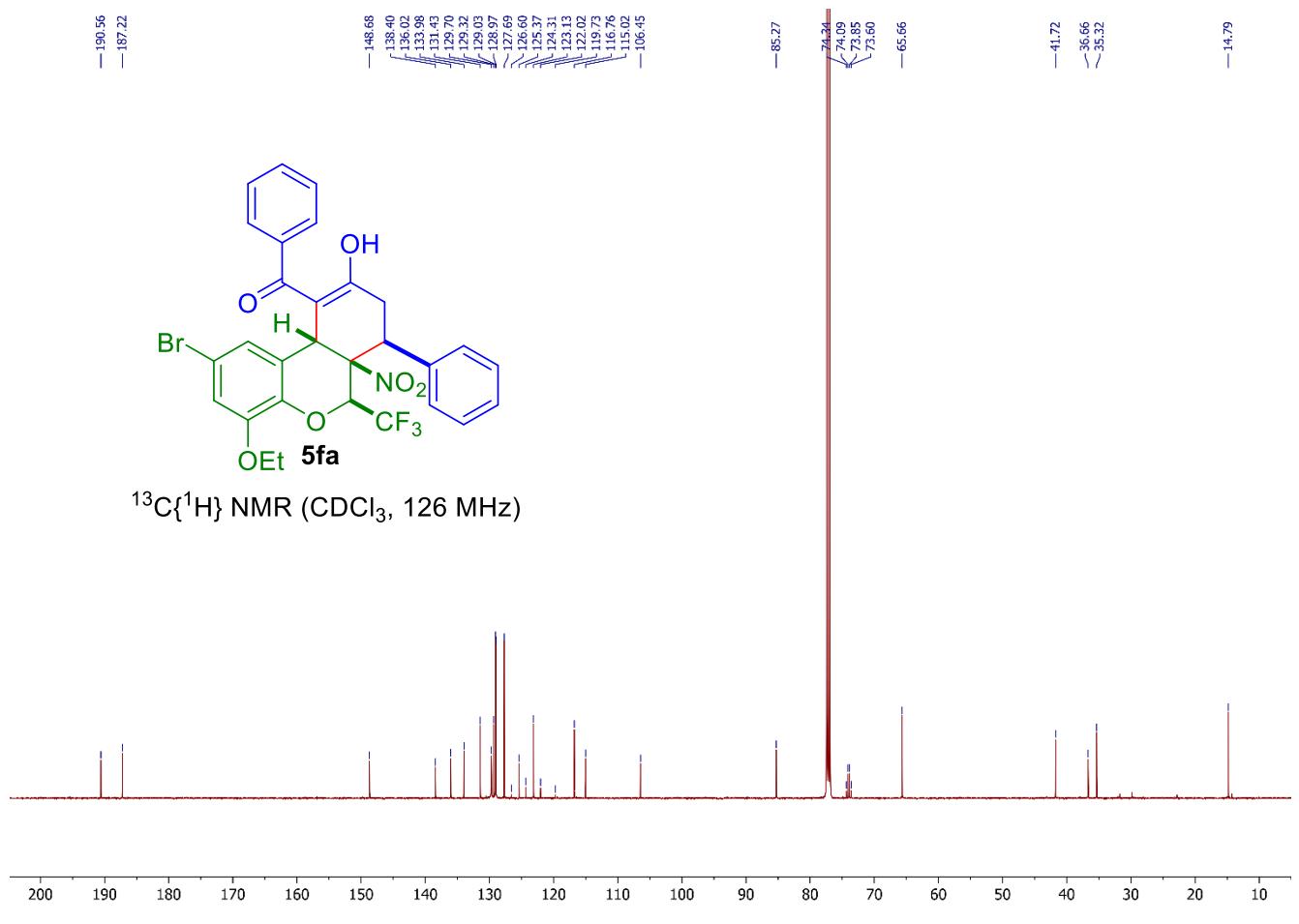
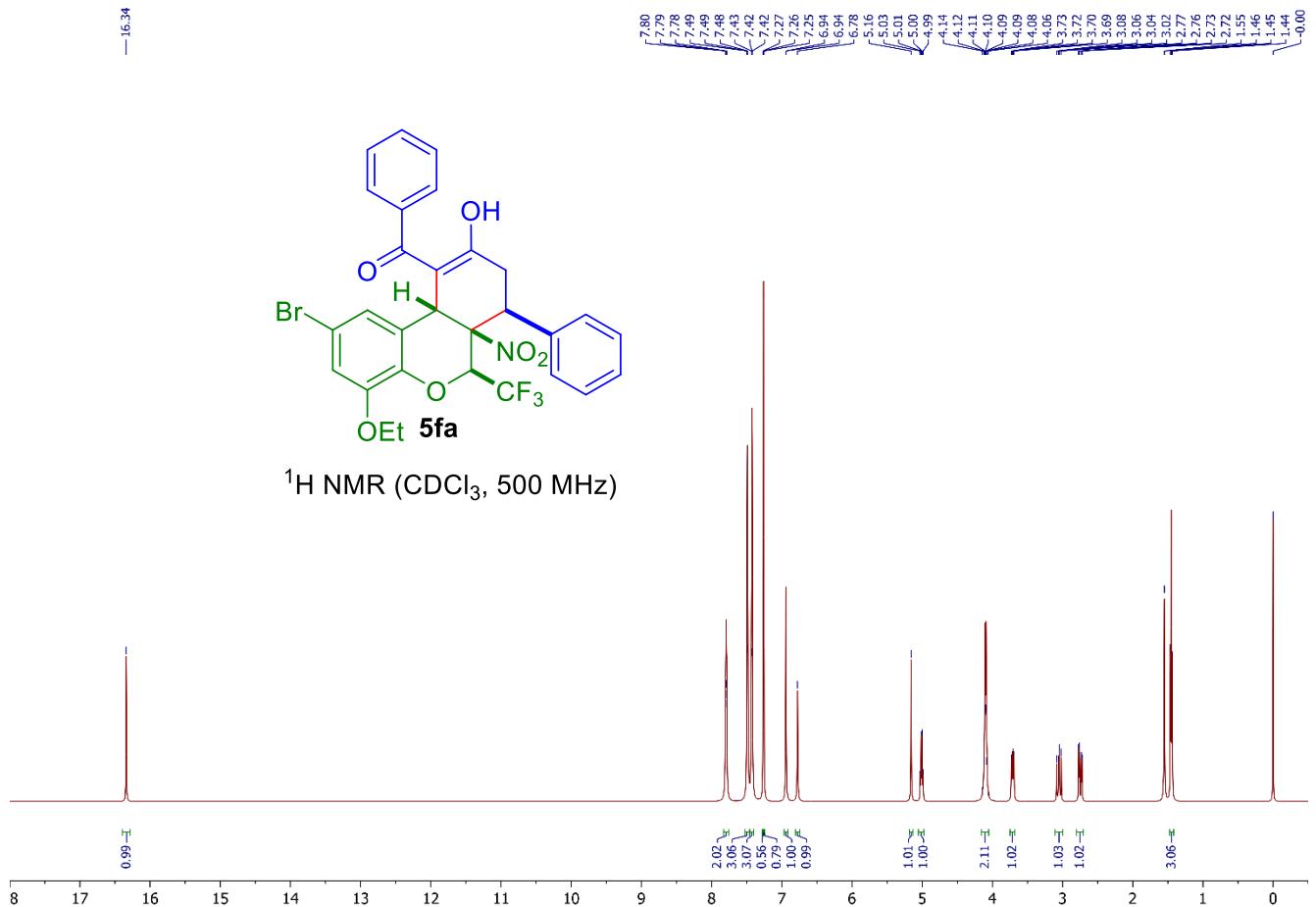


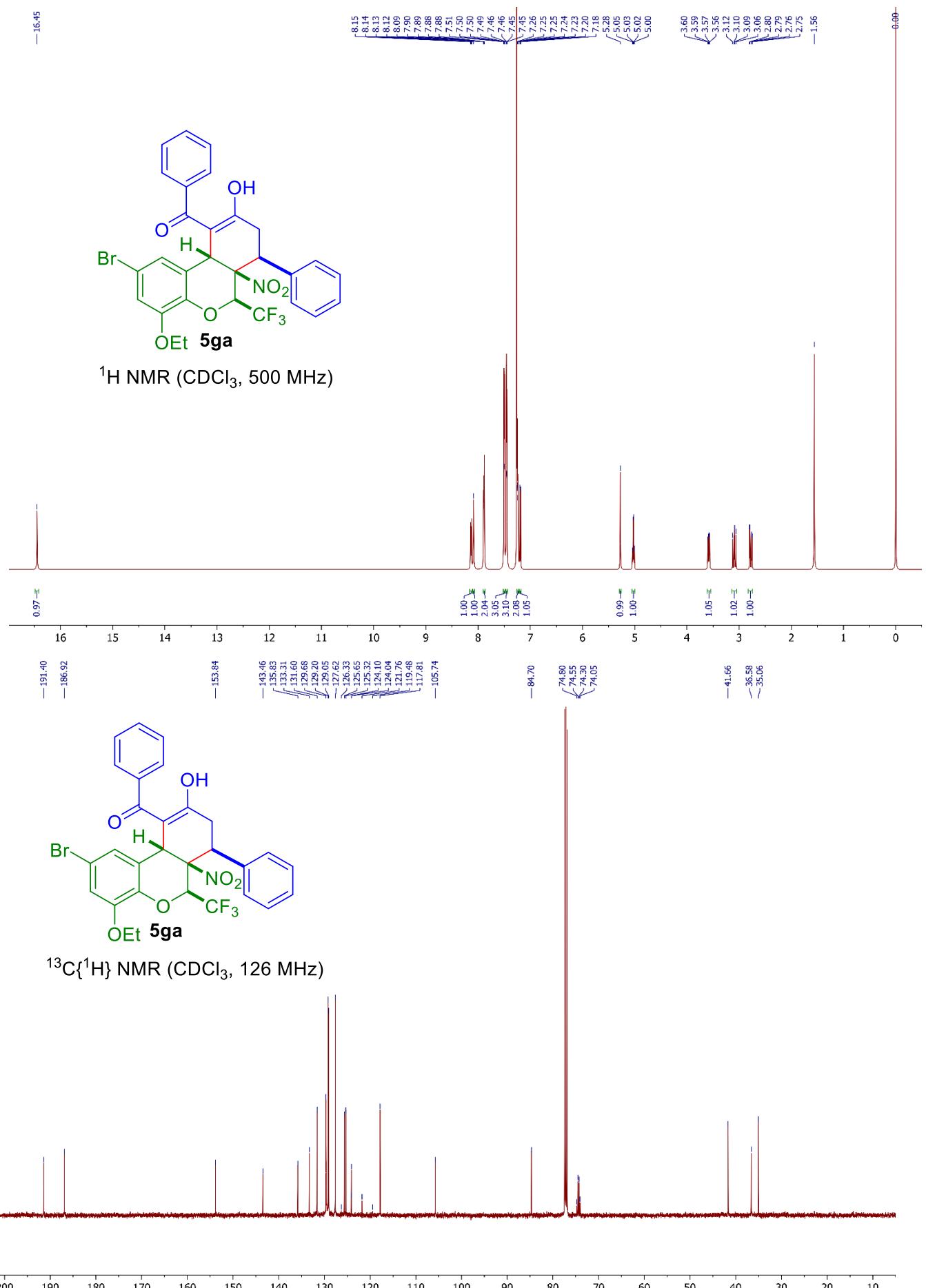


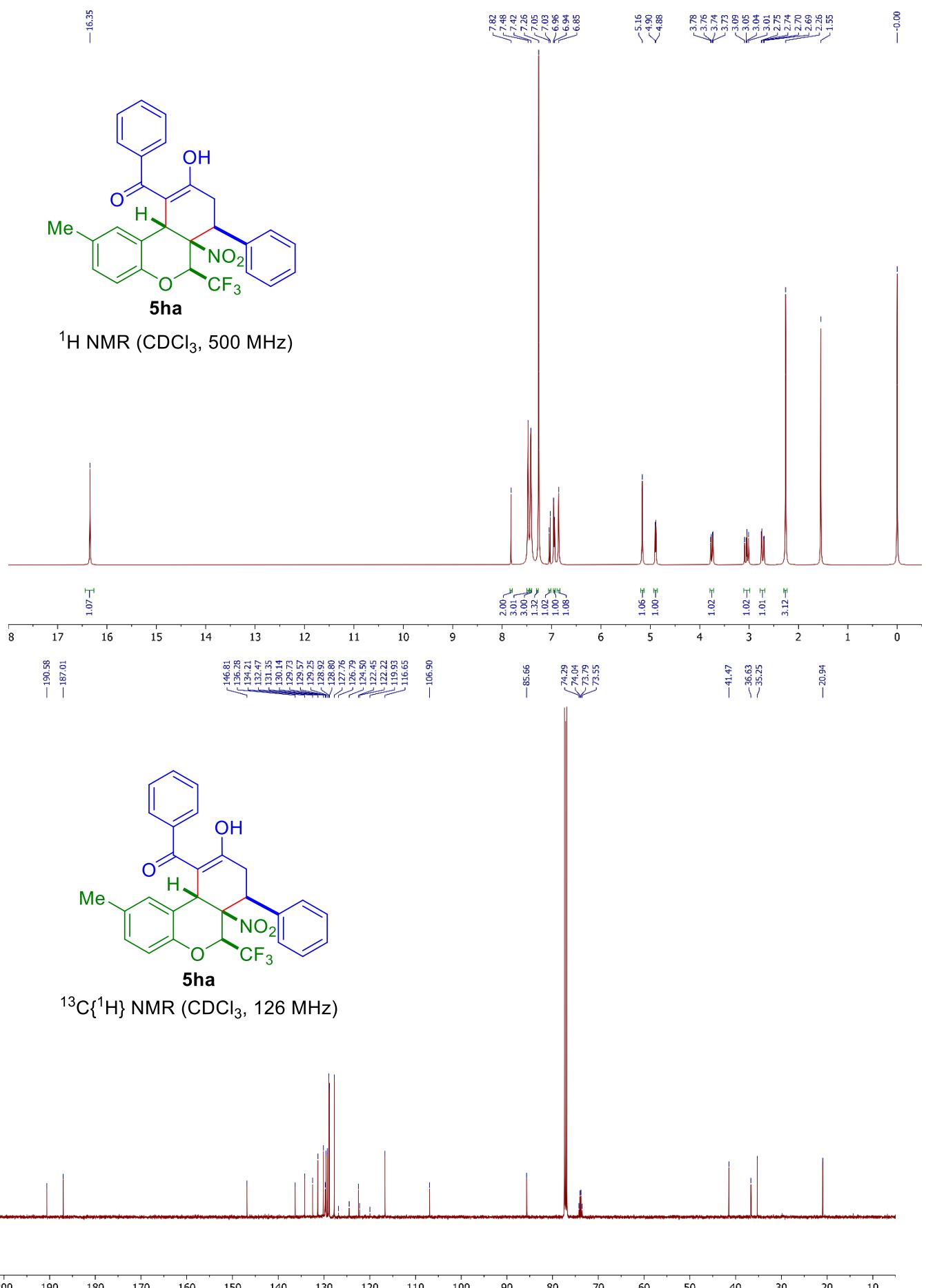


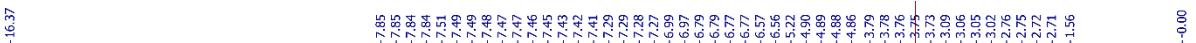




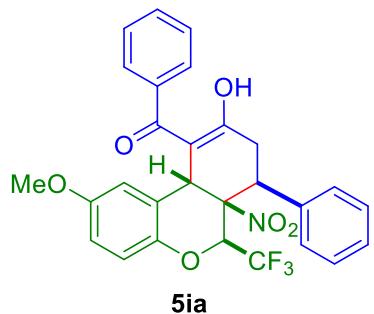
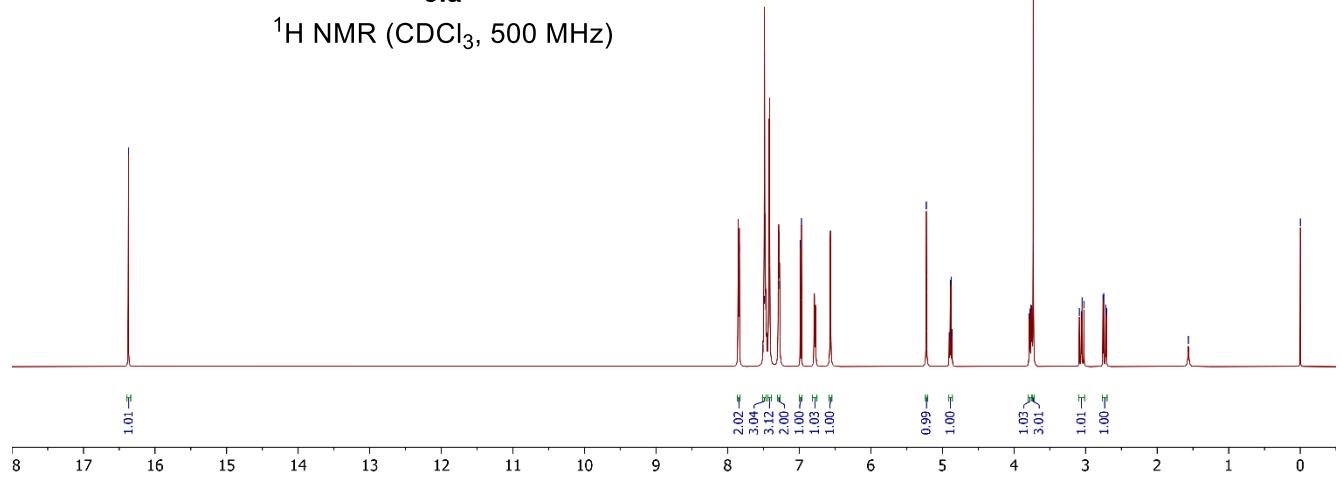




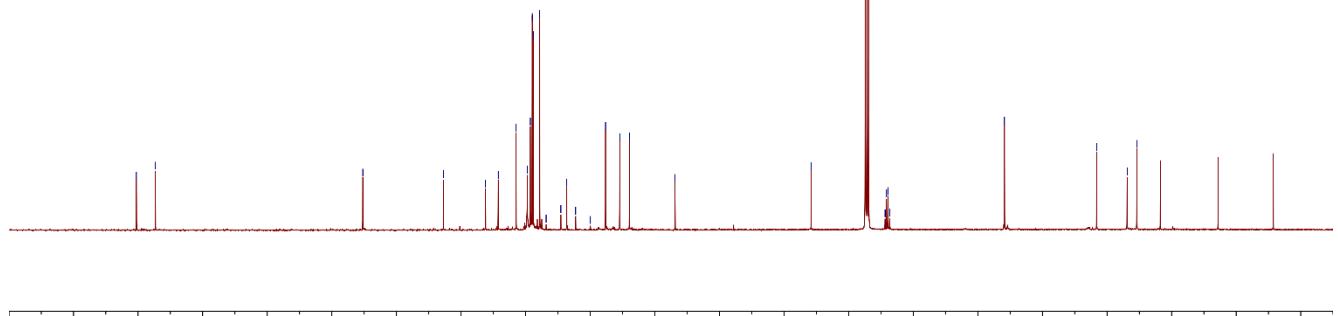


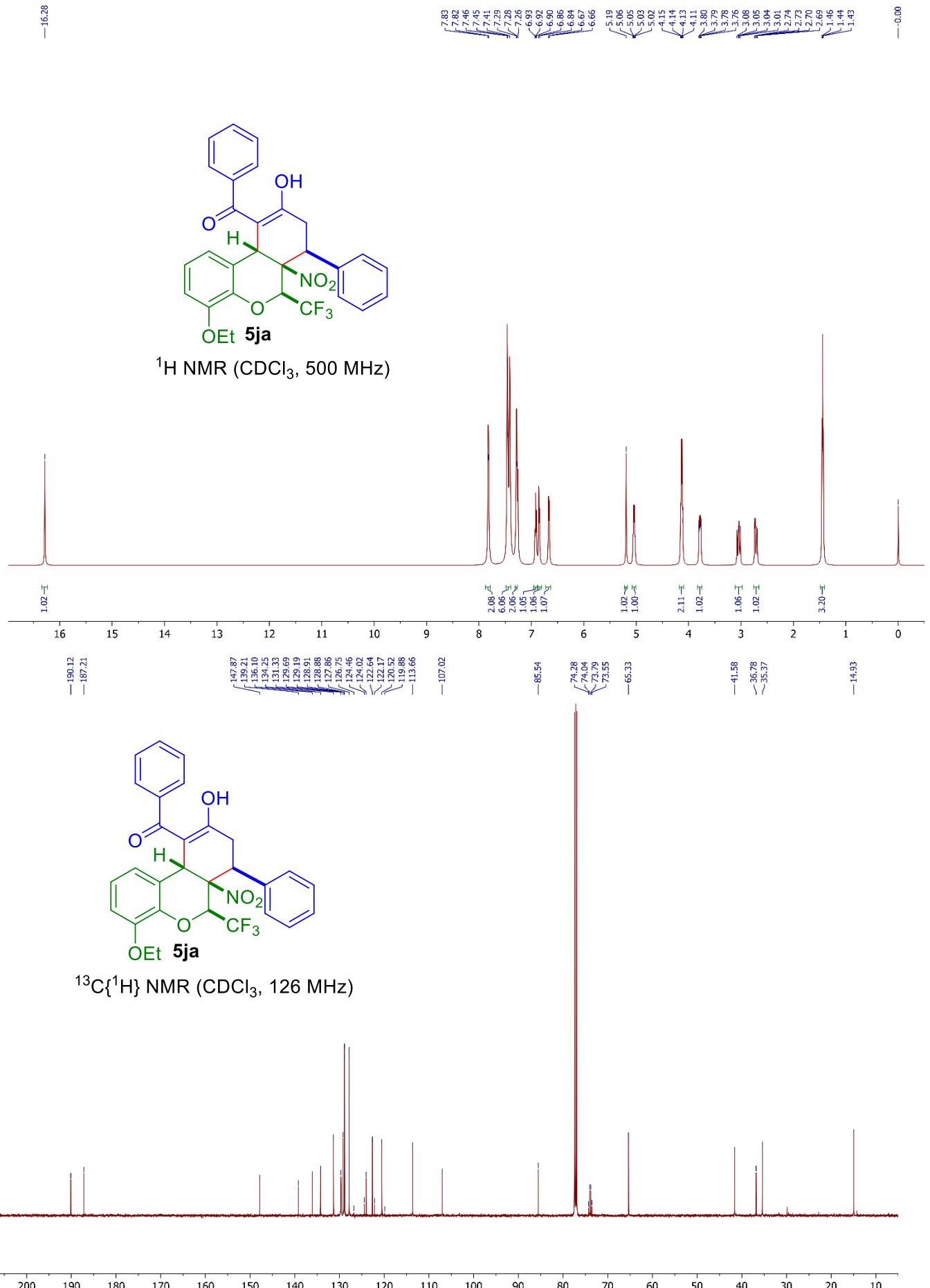


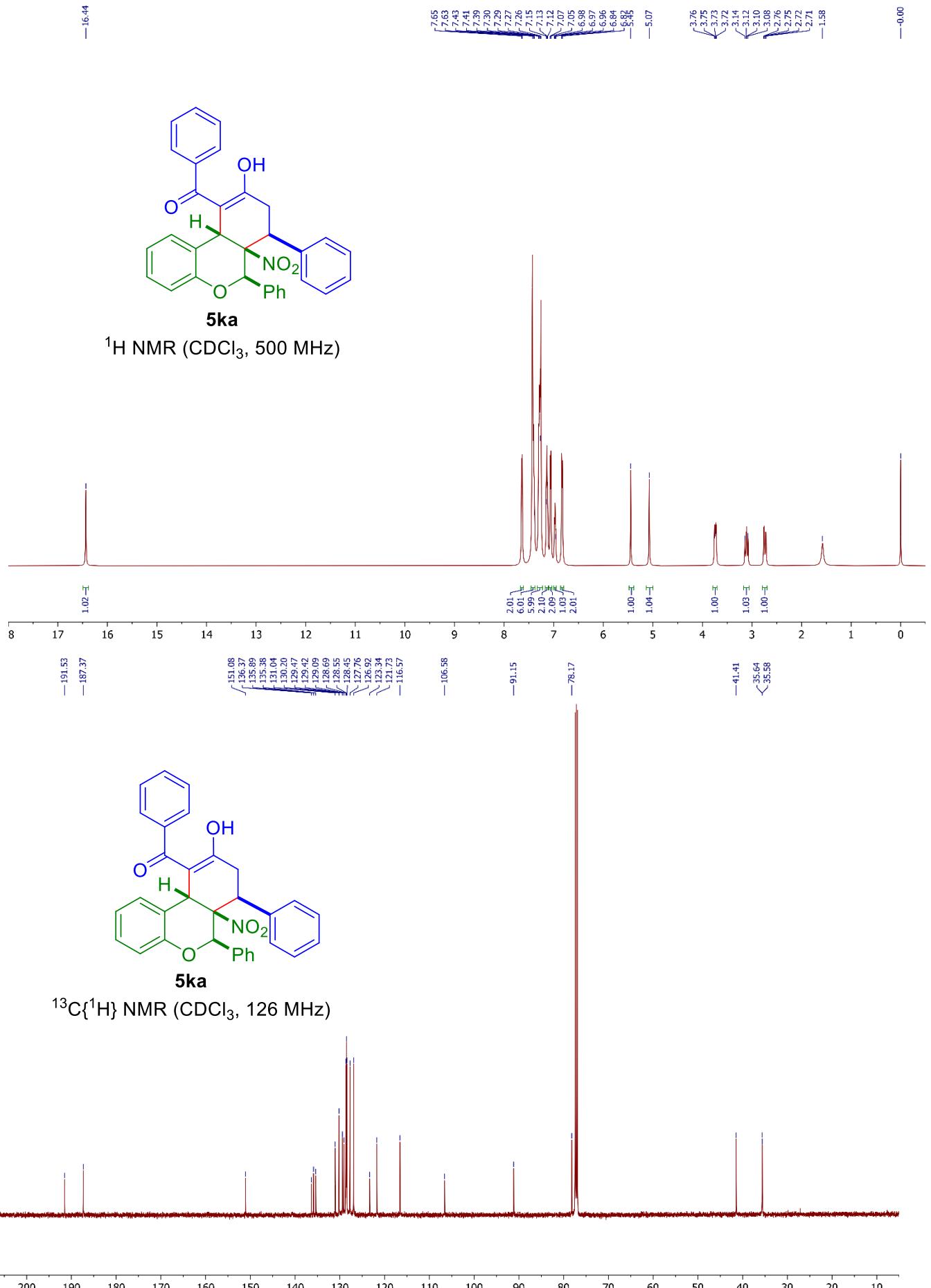
5ia
 ^1H NMR (CDCl_3 , 500 MHz)

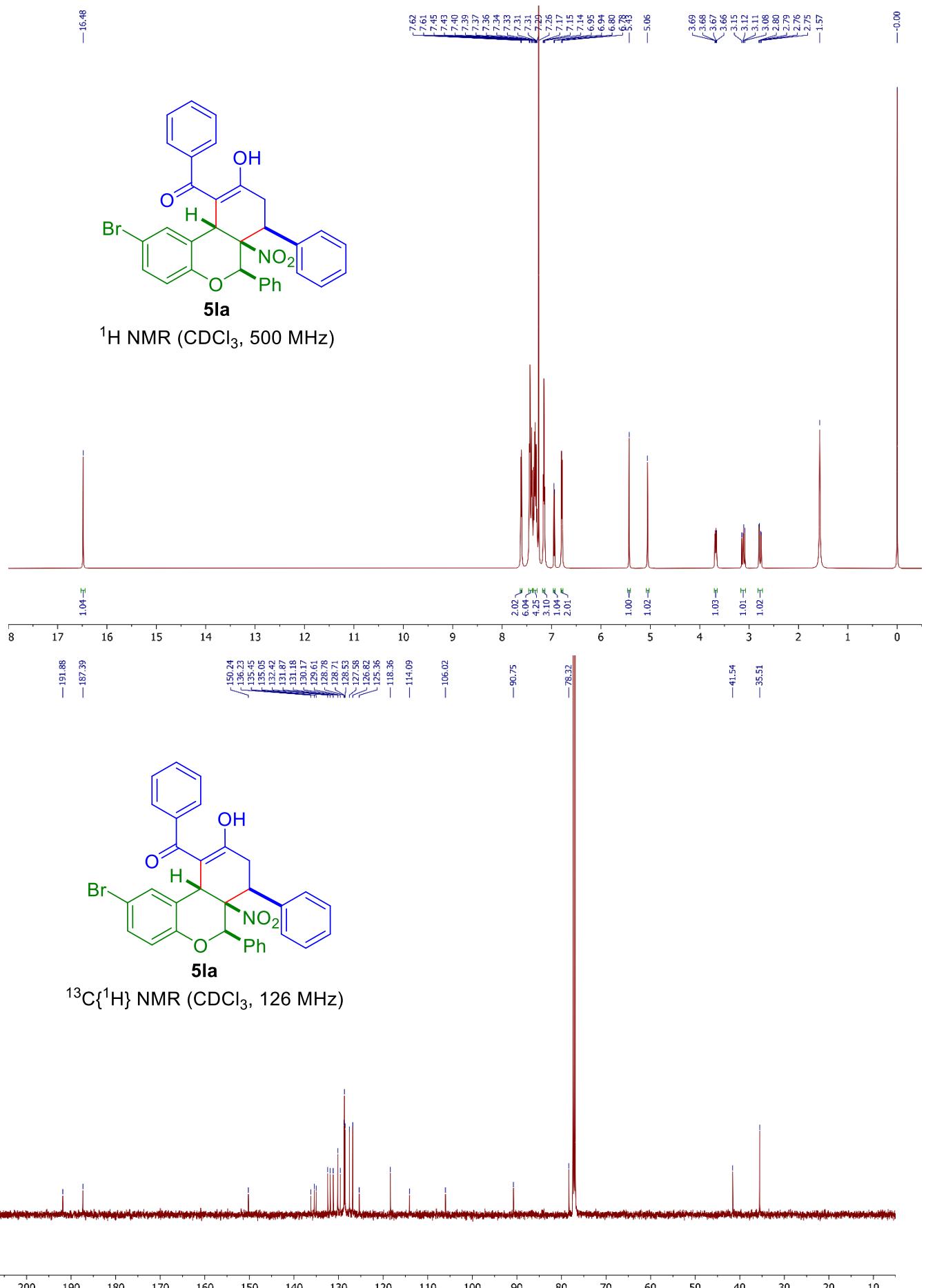


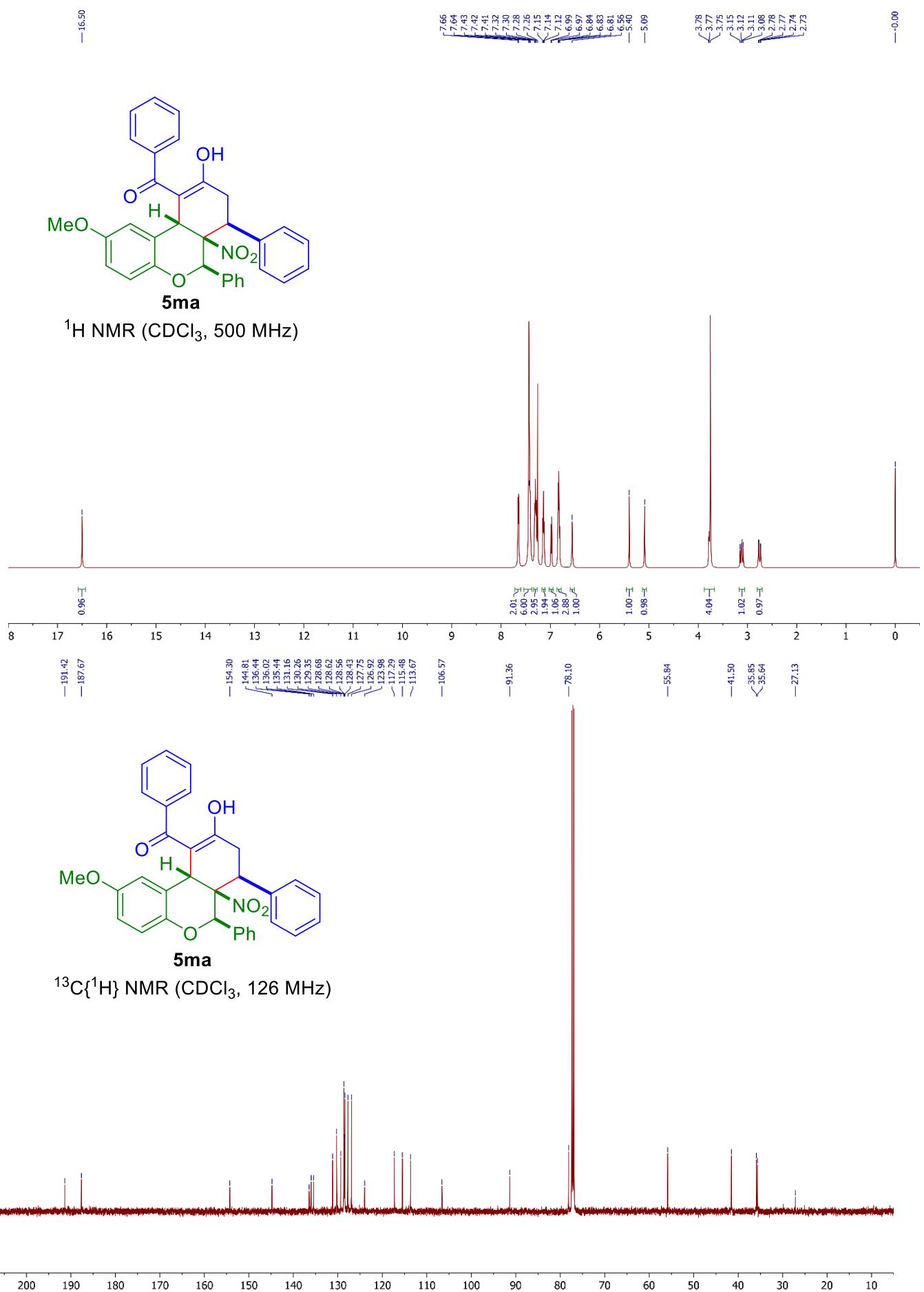
5ia
 $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz)

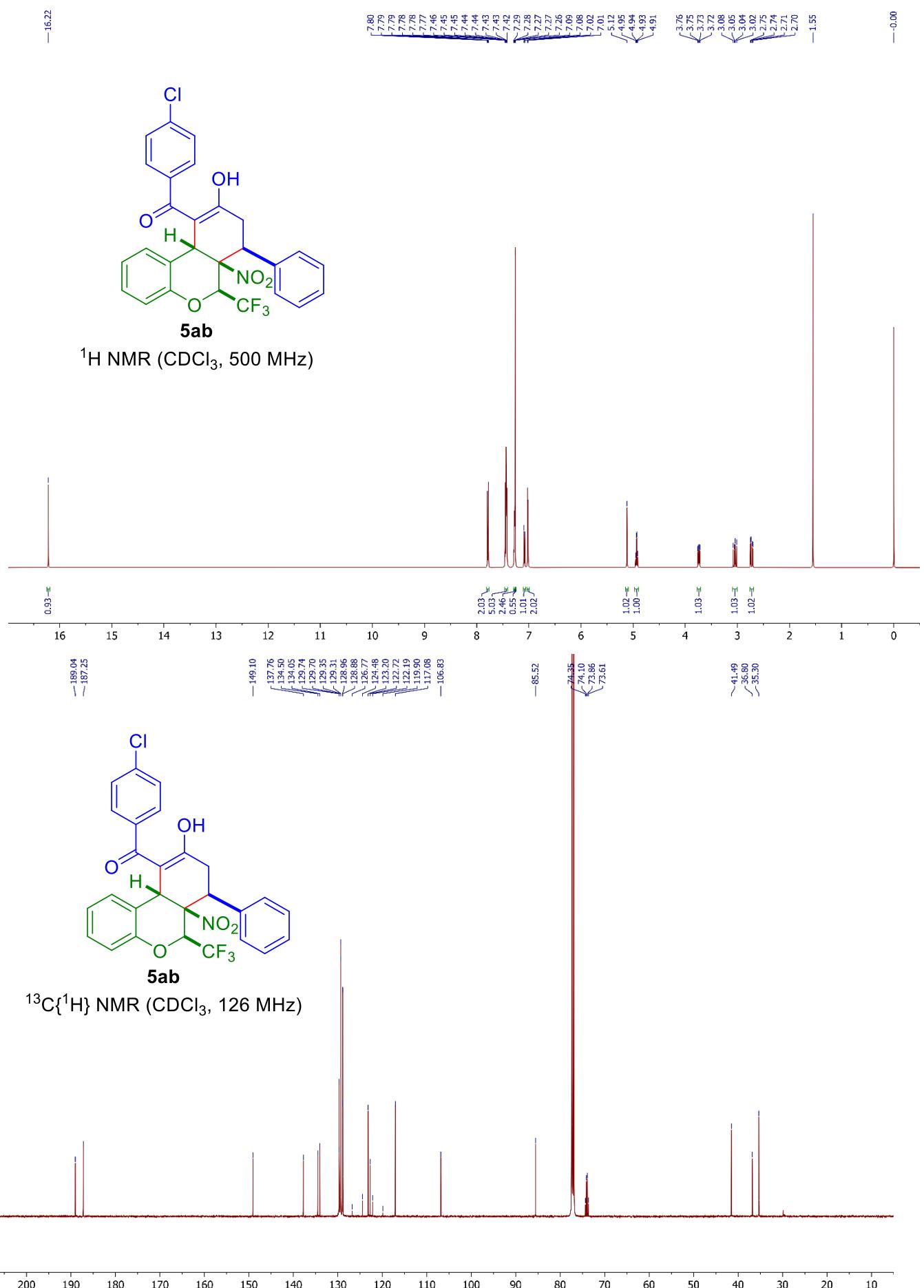


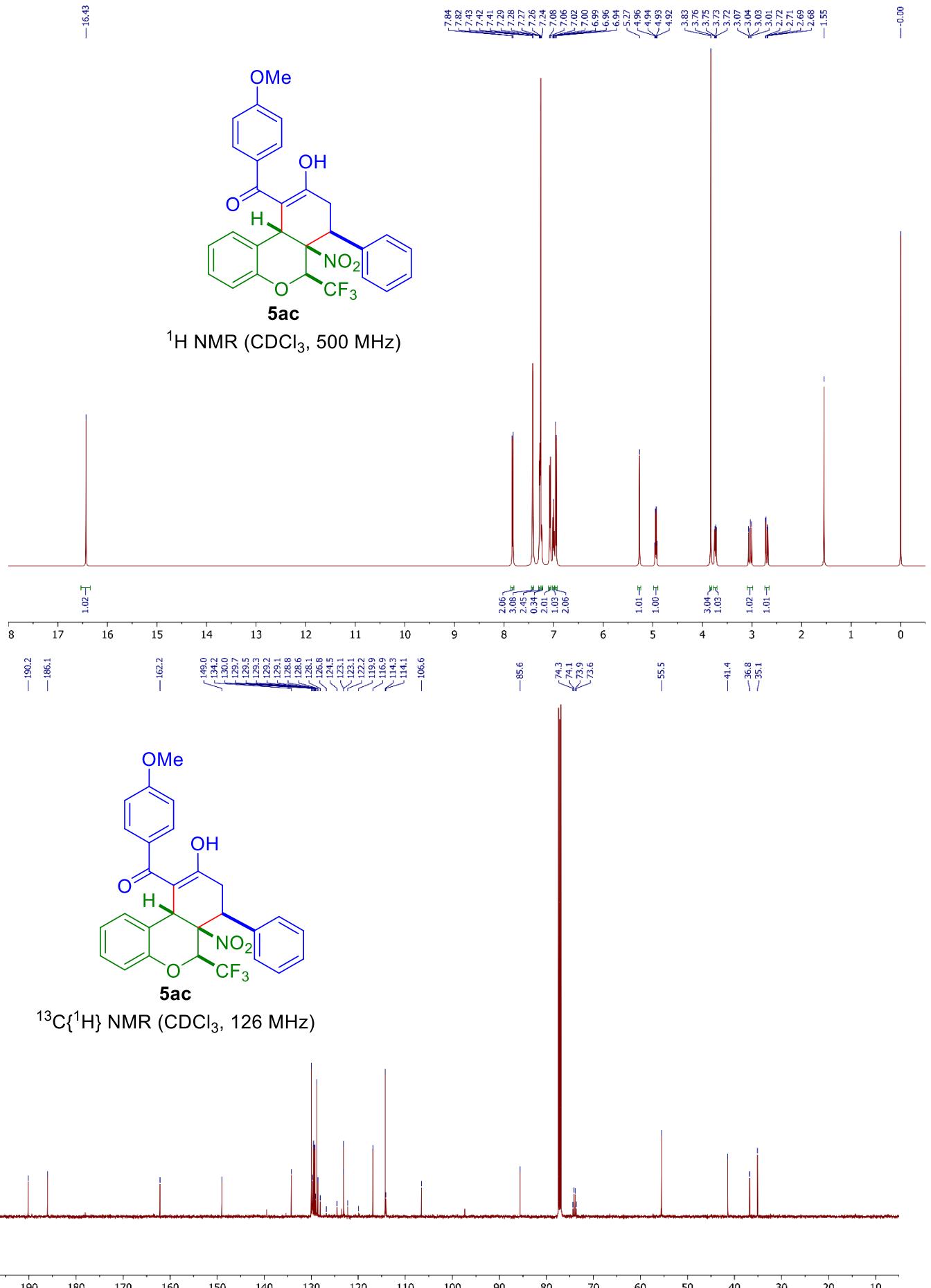


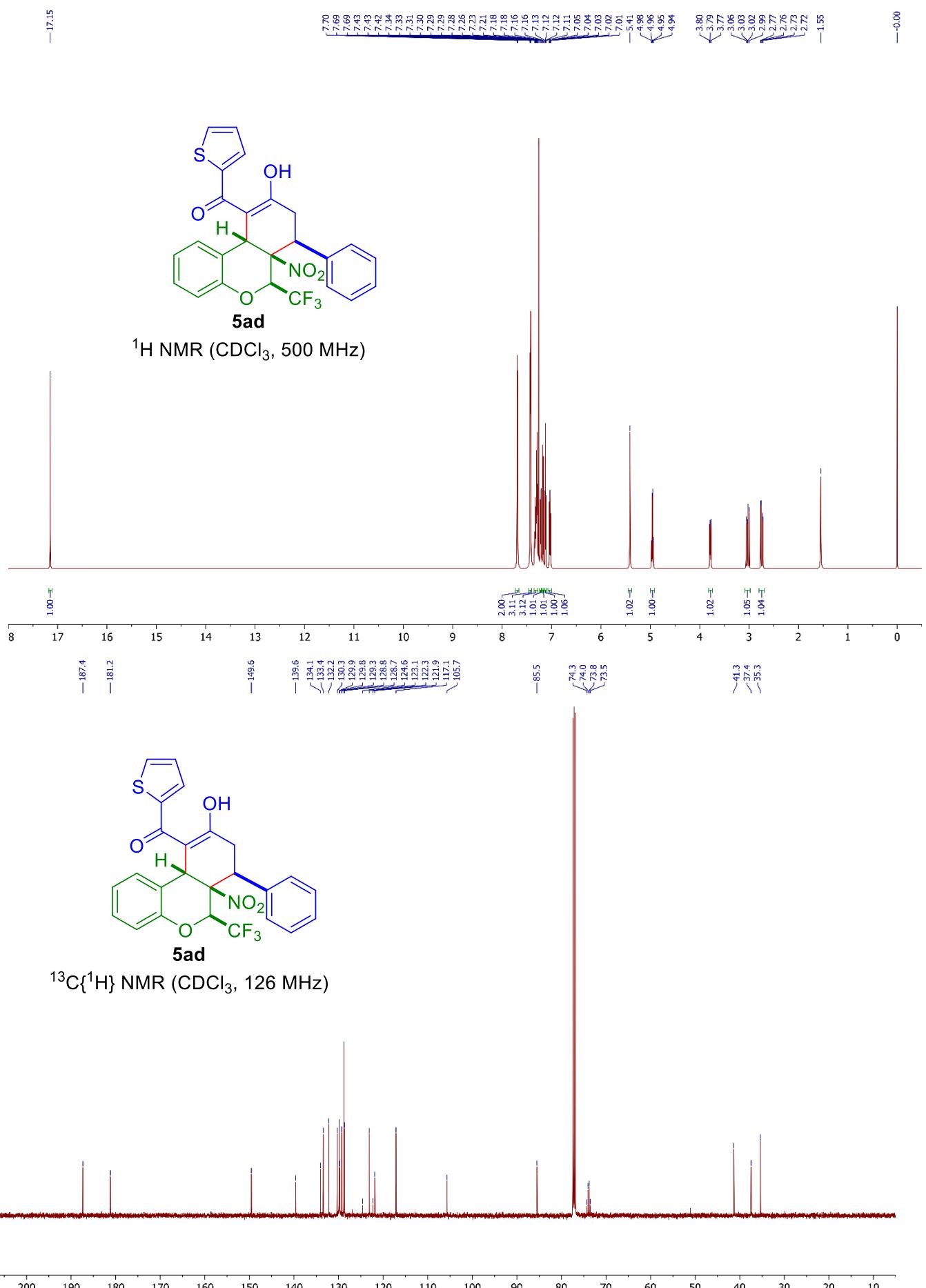


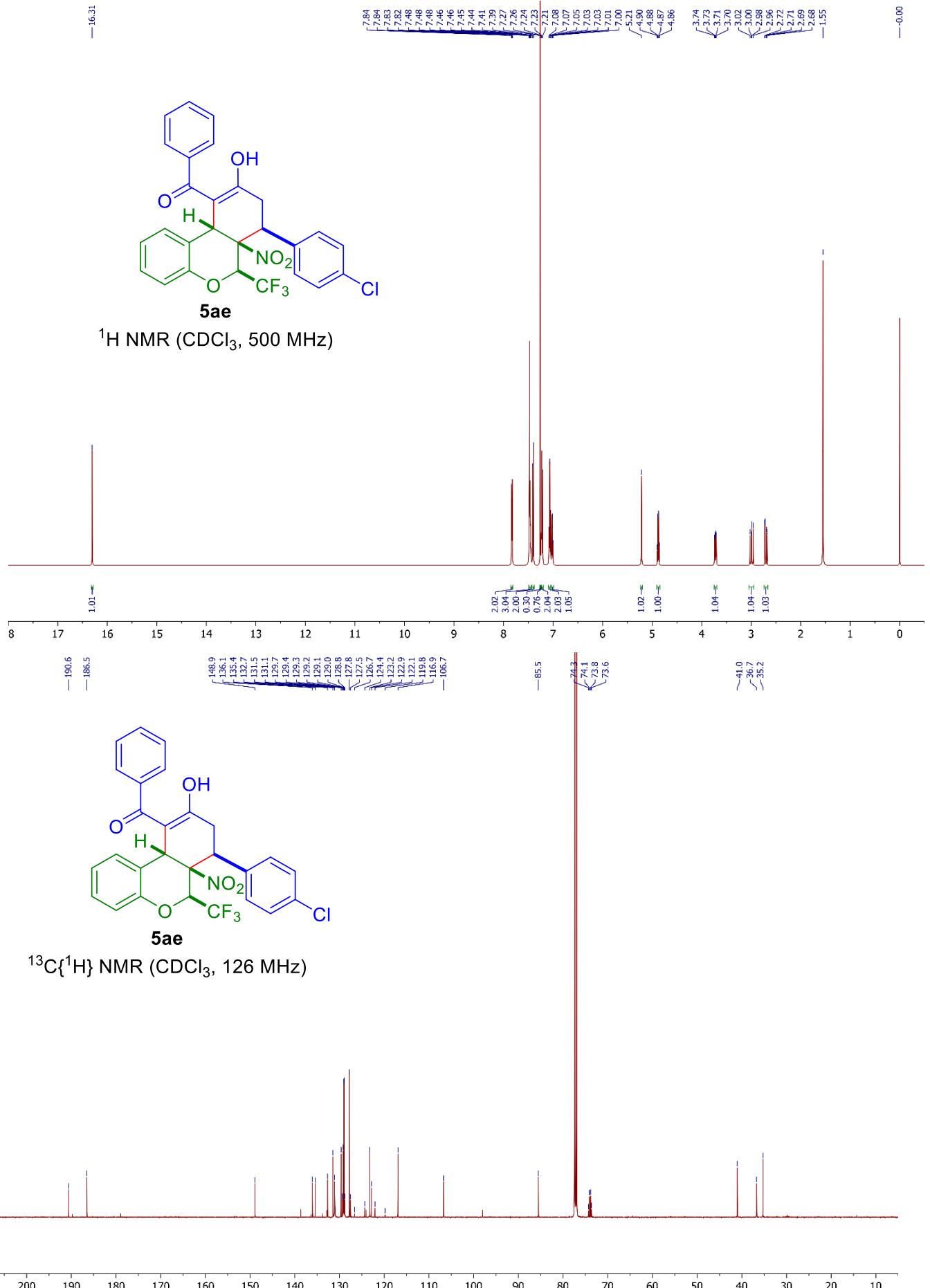


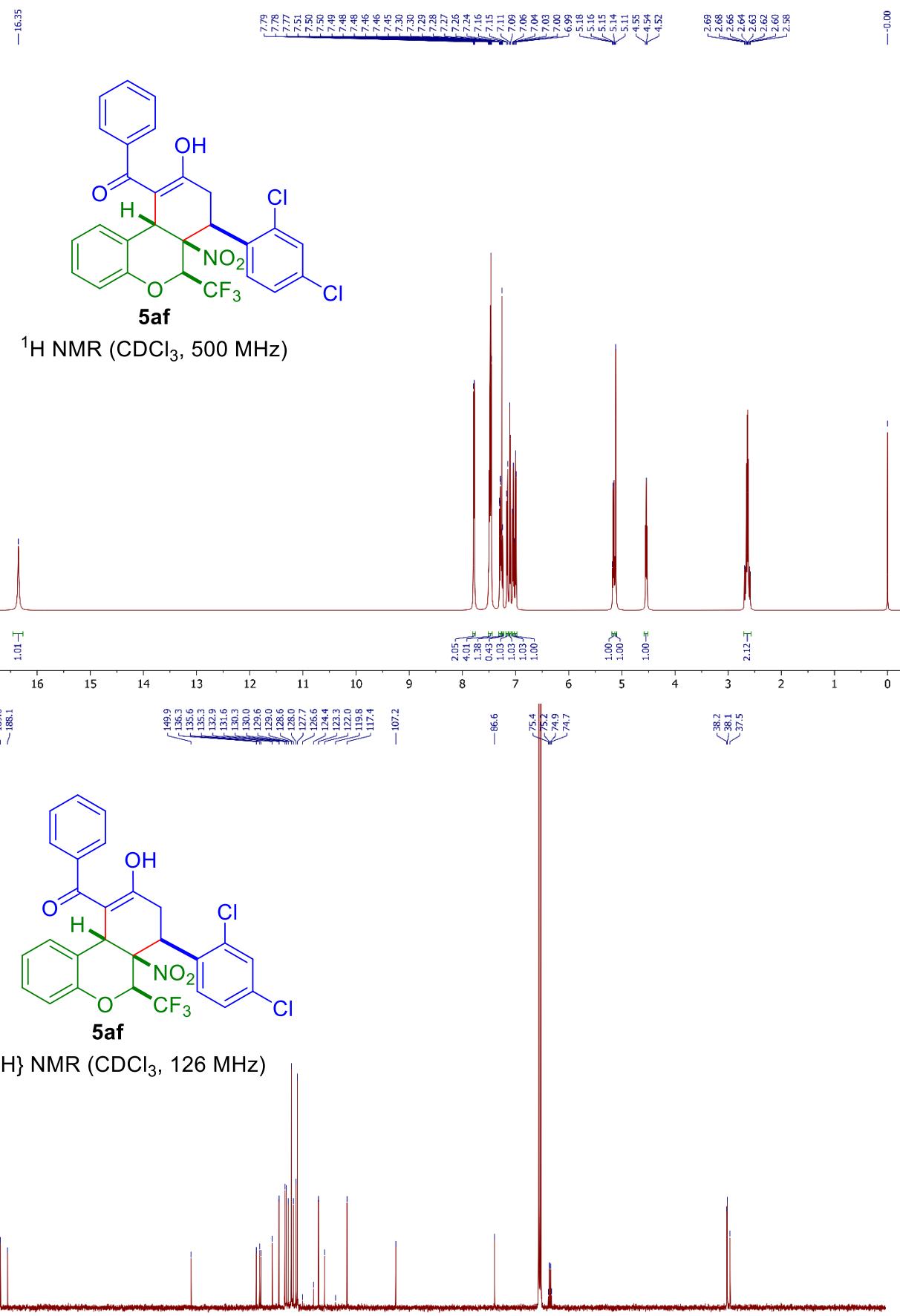


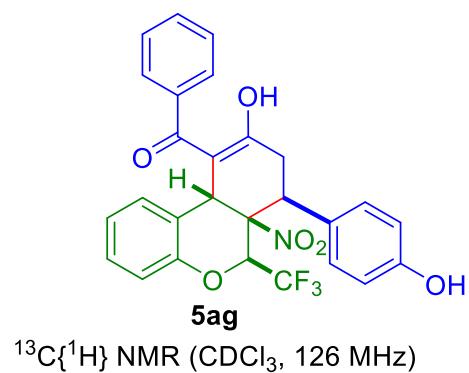
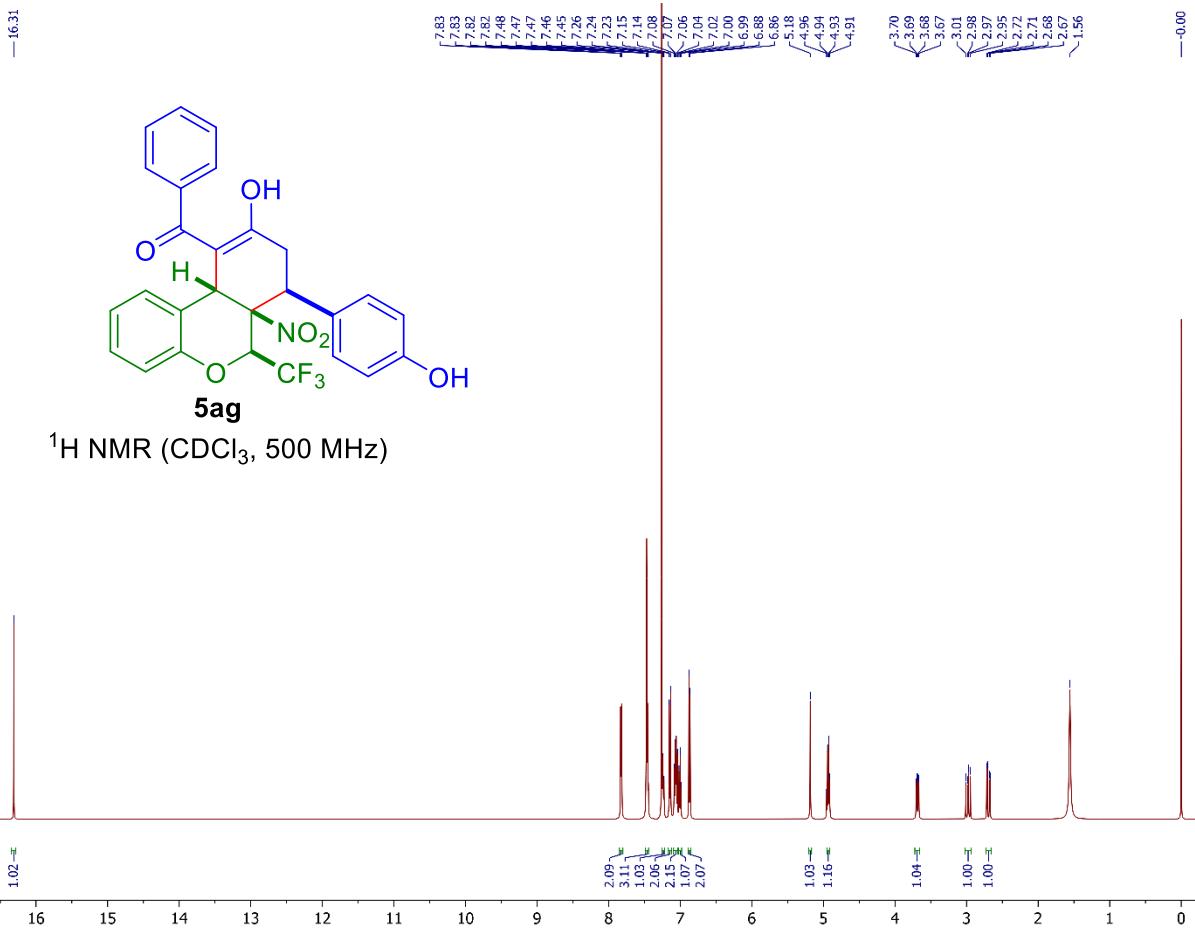






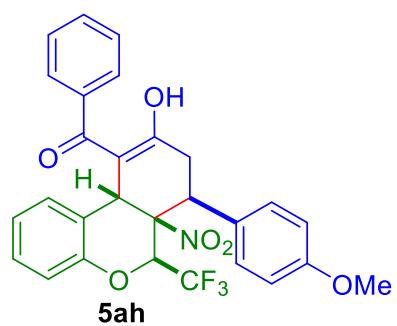




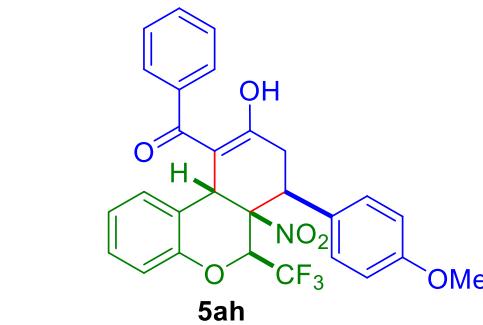
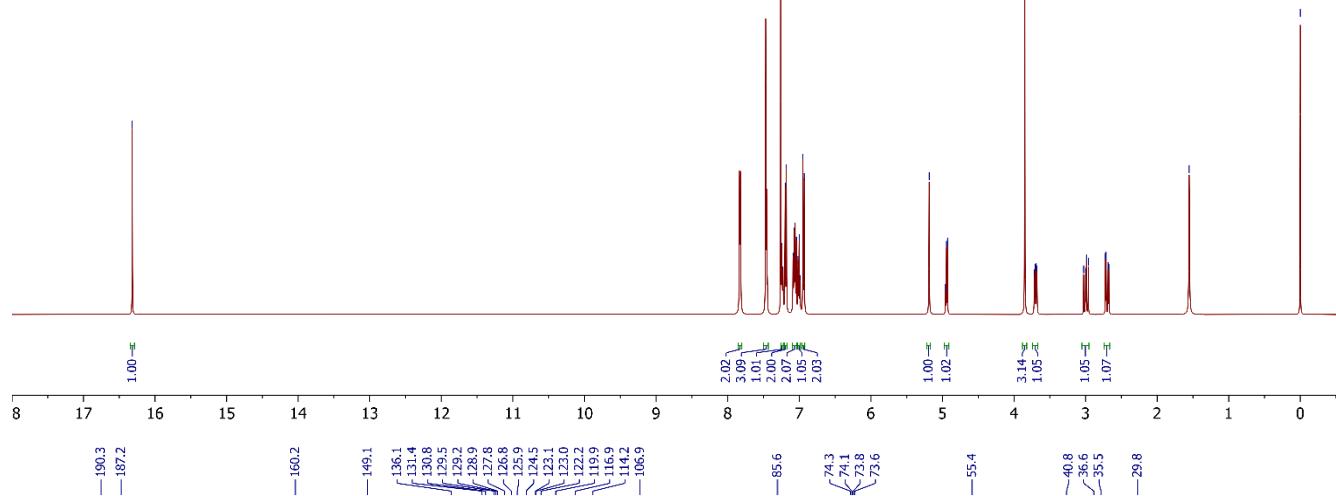


—16.32

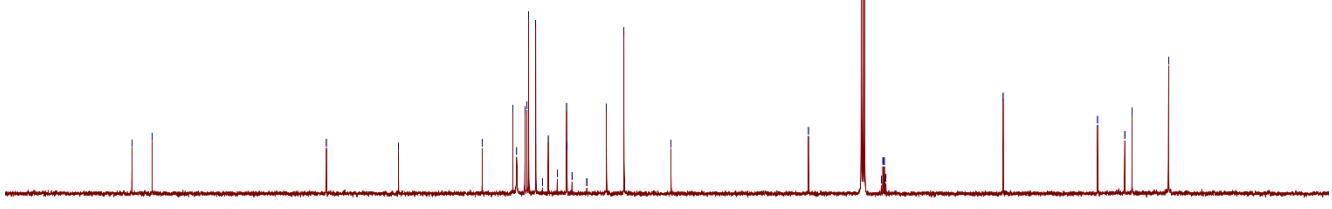
7.84
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7.26
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7.09
7.07
7.06
7.04
7.02
7.01
7.00
7.00
6.99
6.95
6.93
5.19
4.96
4.94
4.93
3.85
3.72
3.69
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1.55
—0.00

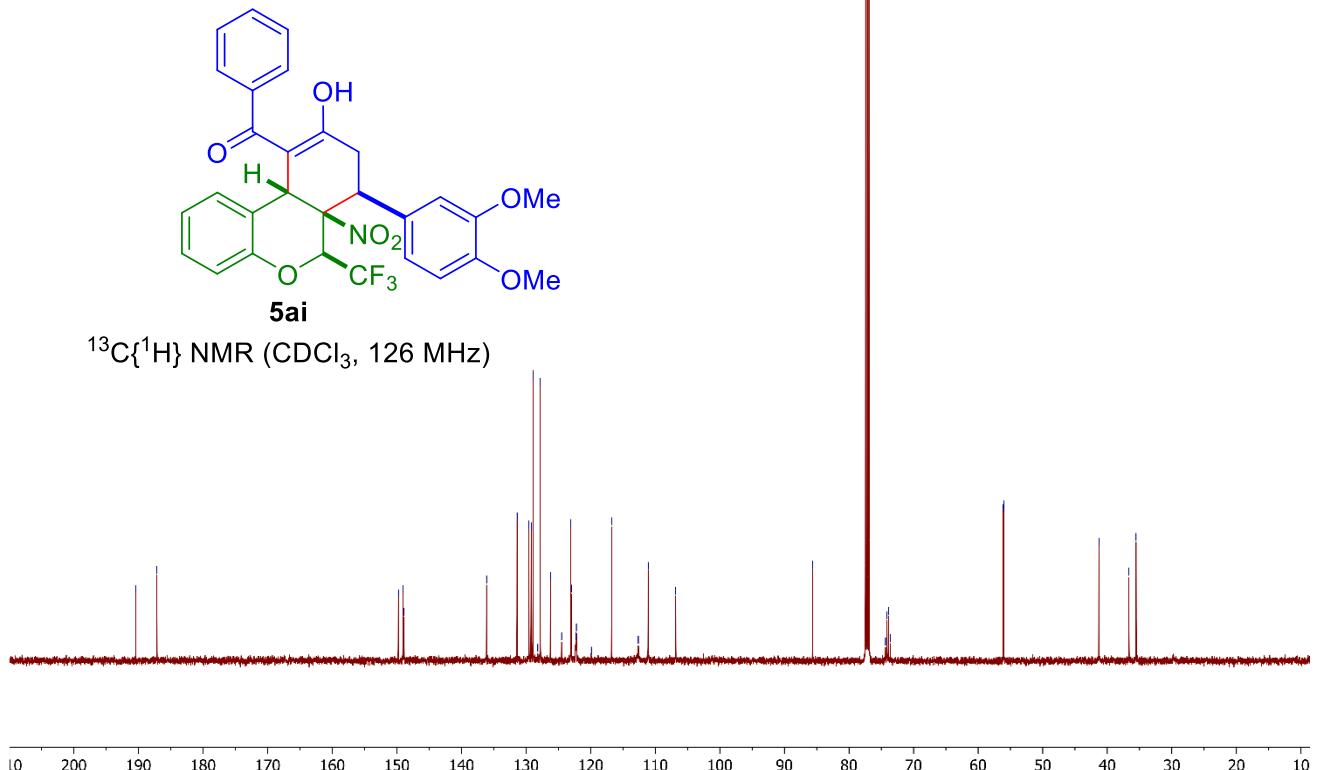
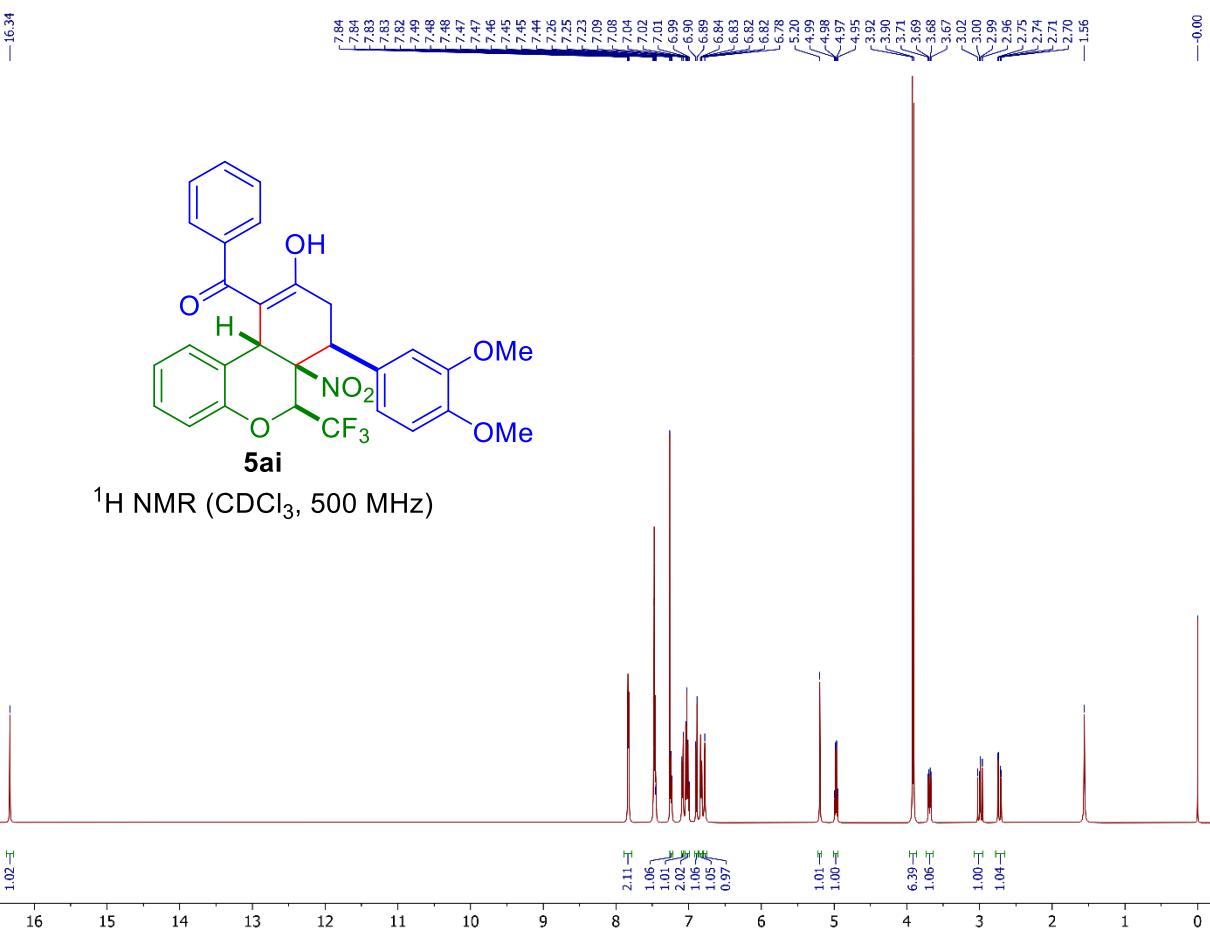


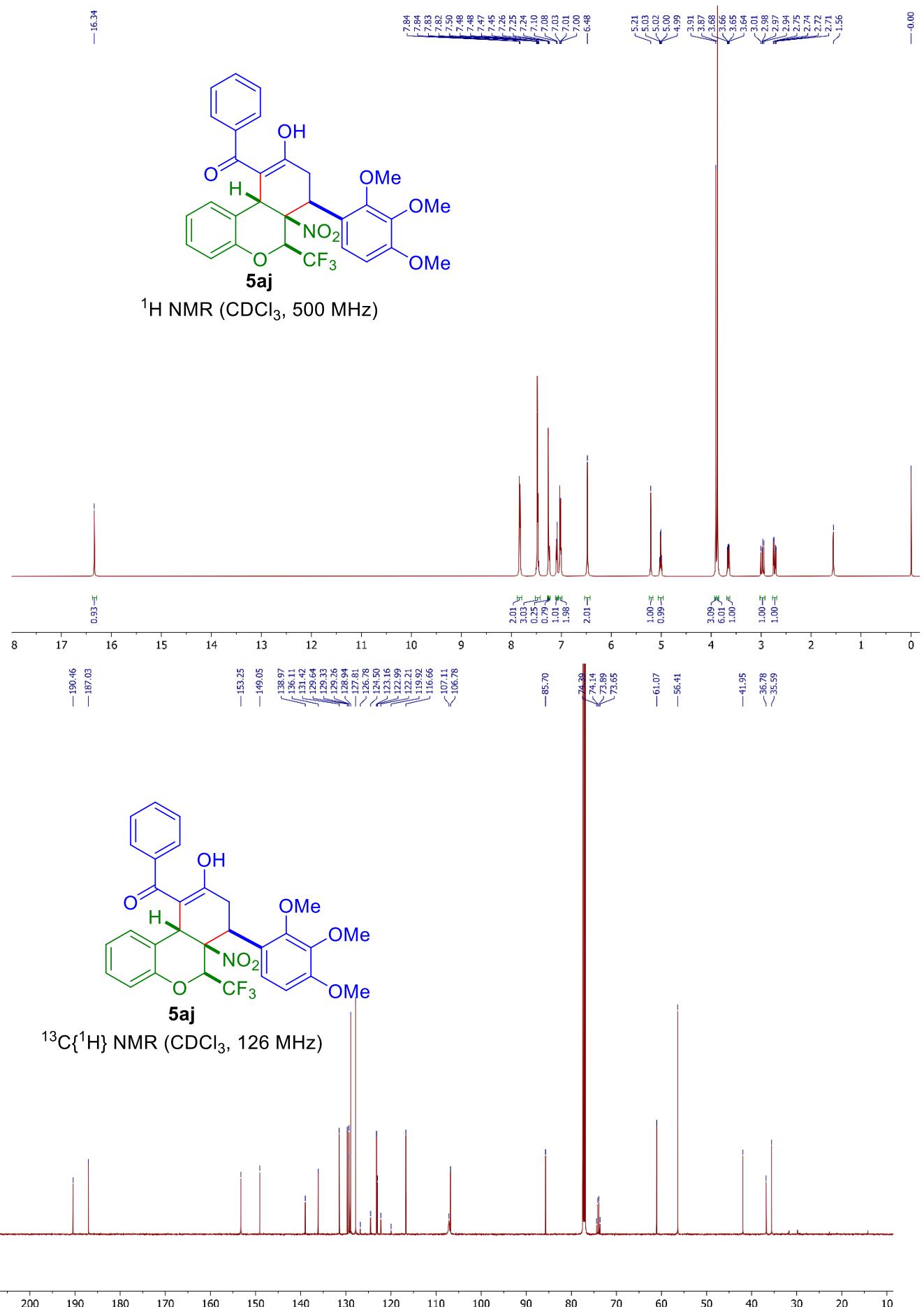
¹H NMR (CDCl₃, 500 MHz)

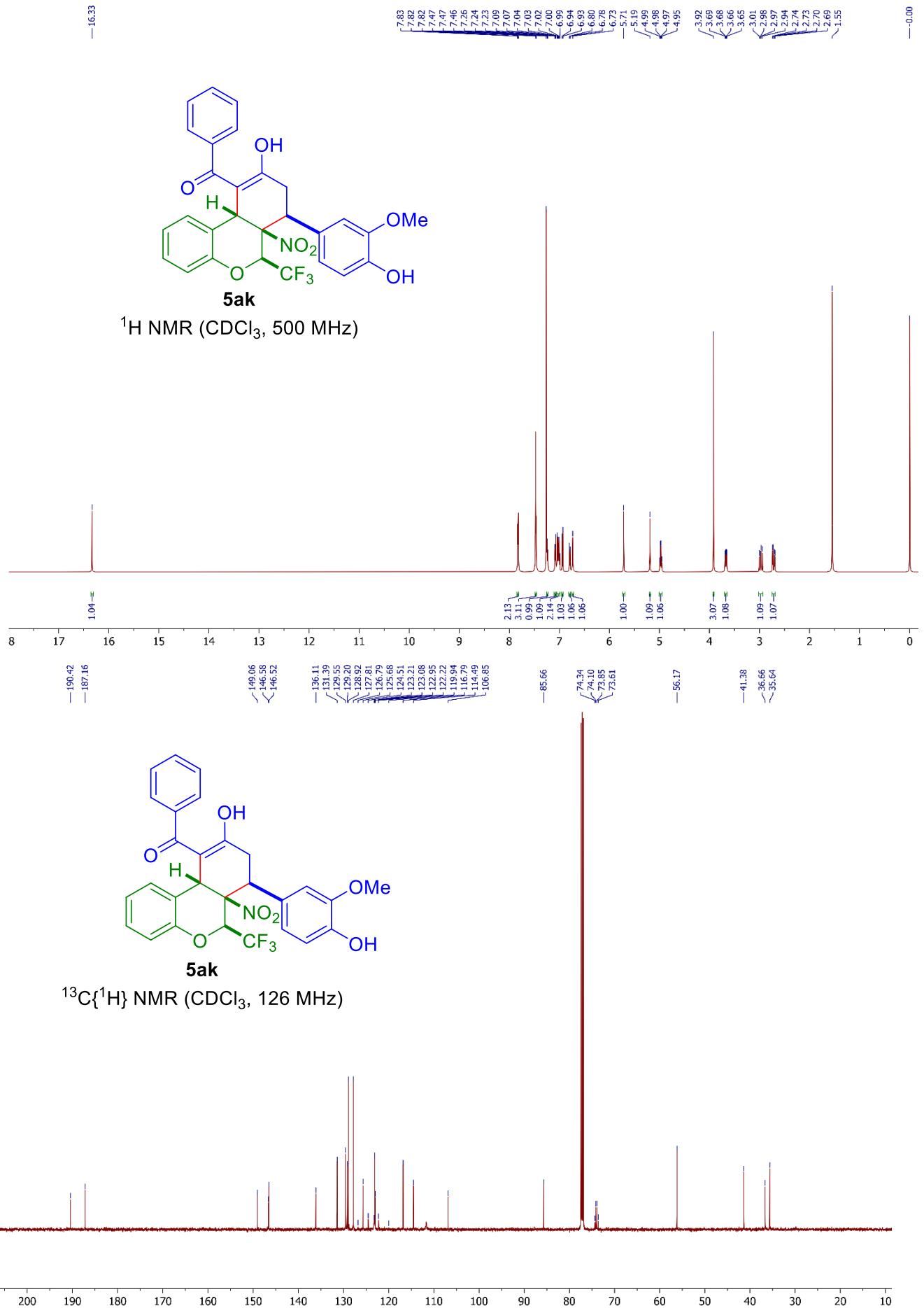


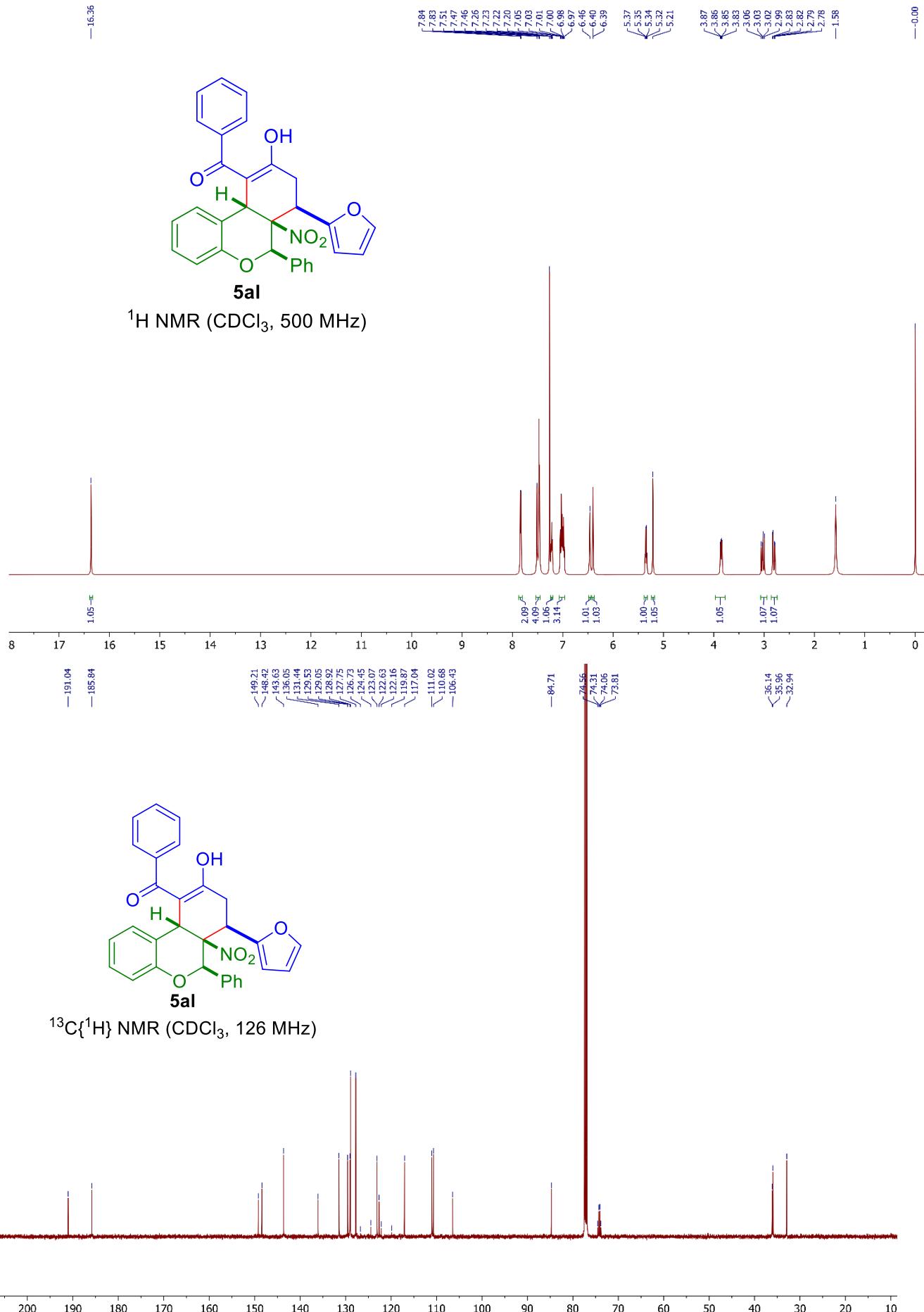
¹³C{¹H} NMR (CDCl₃, 126 MHz)

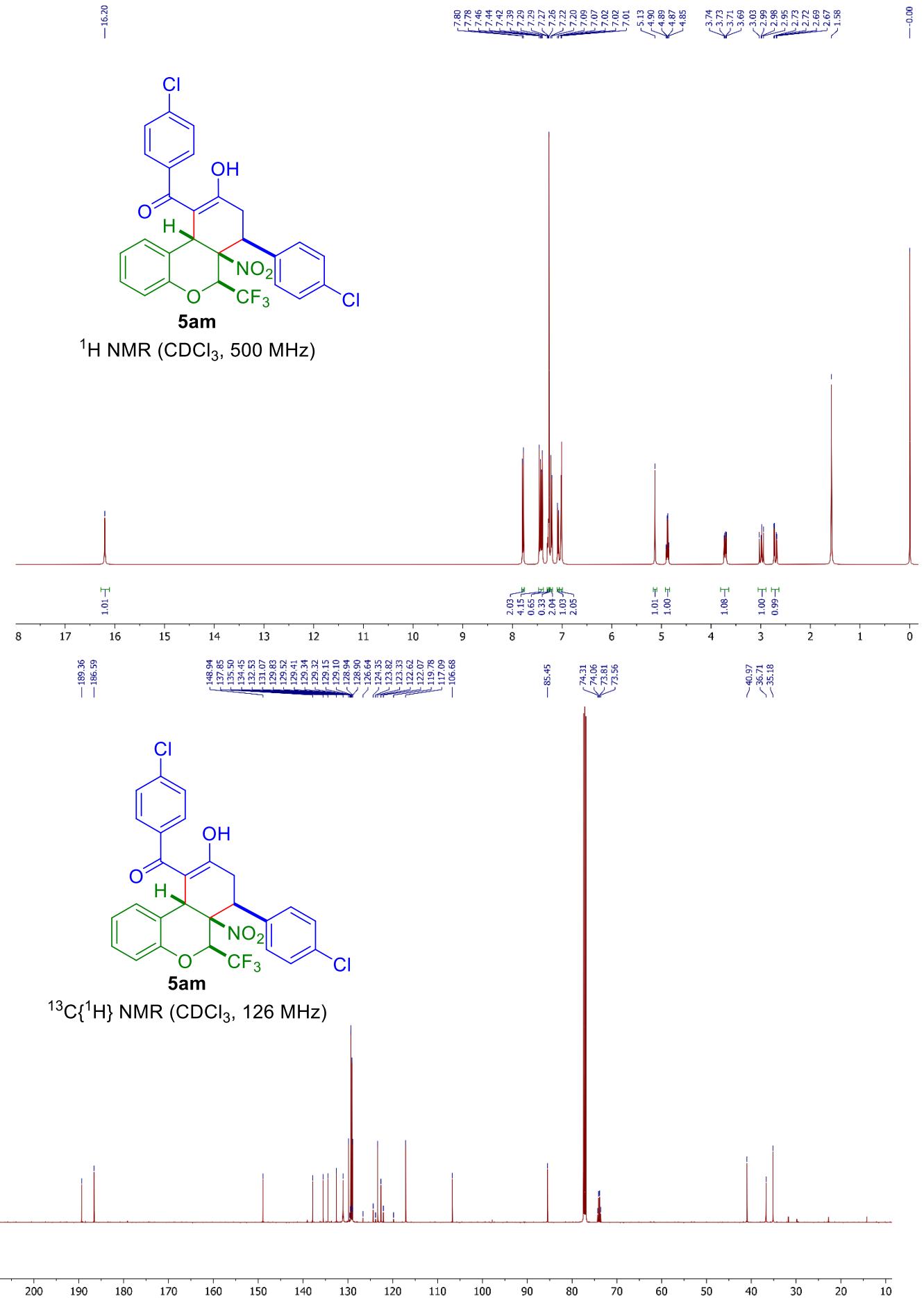


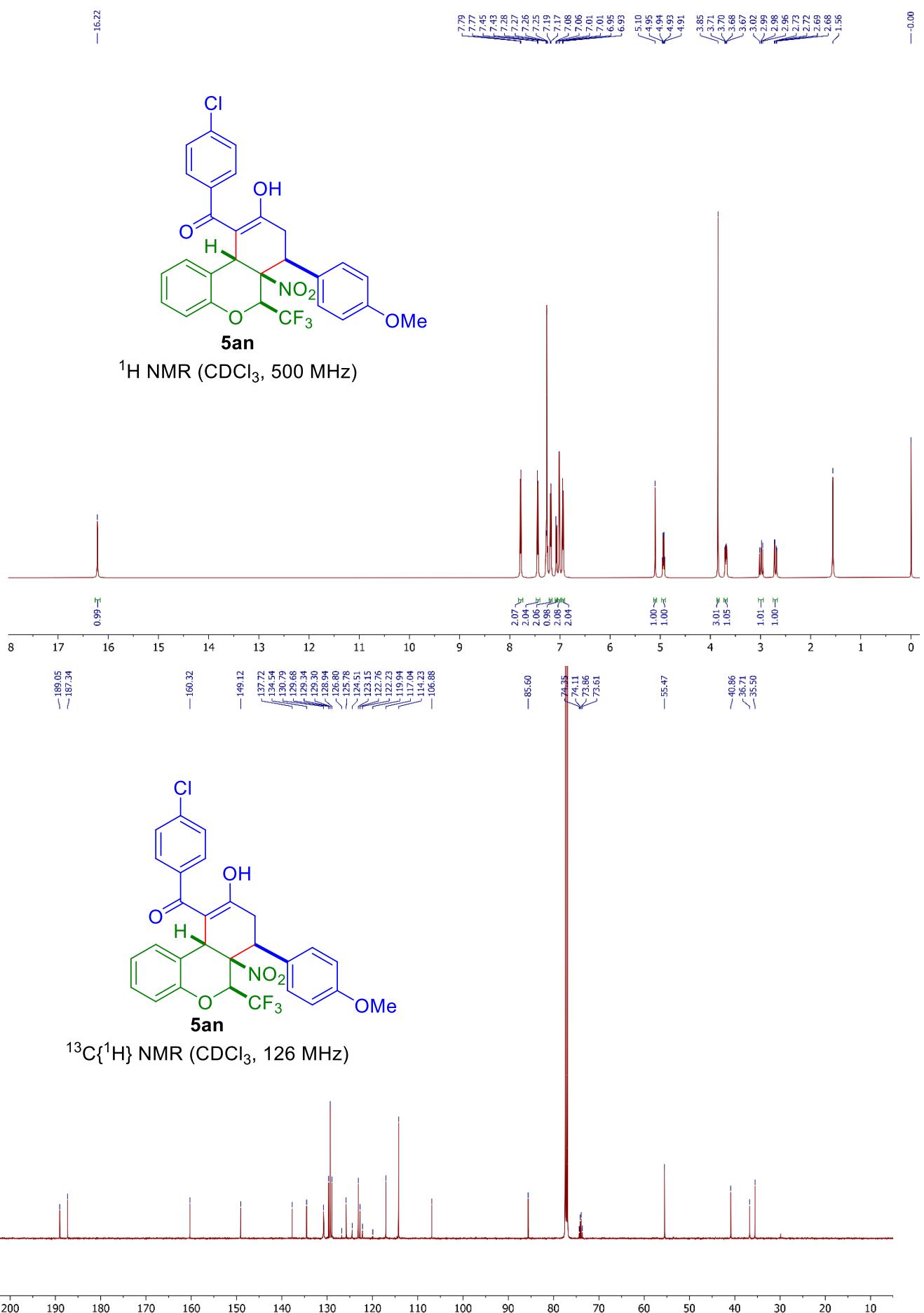


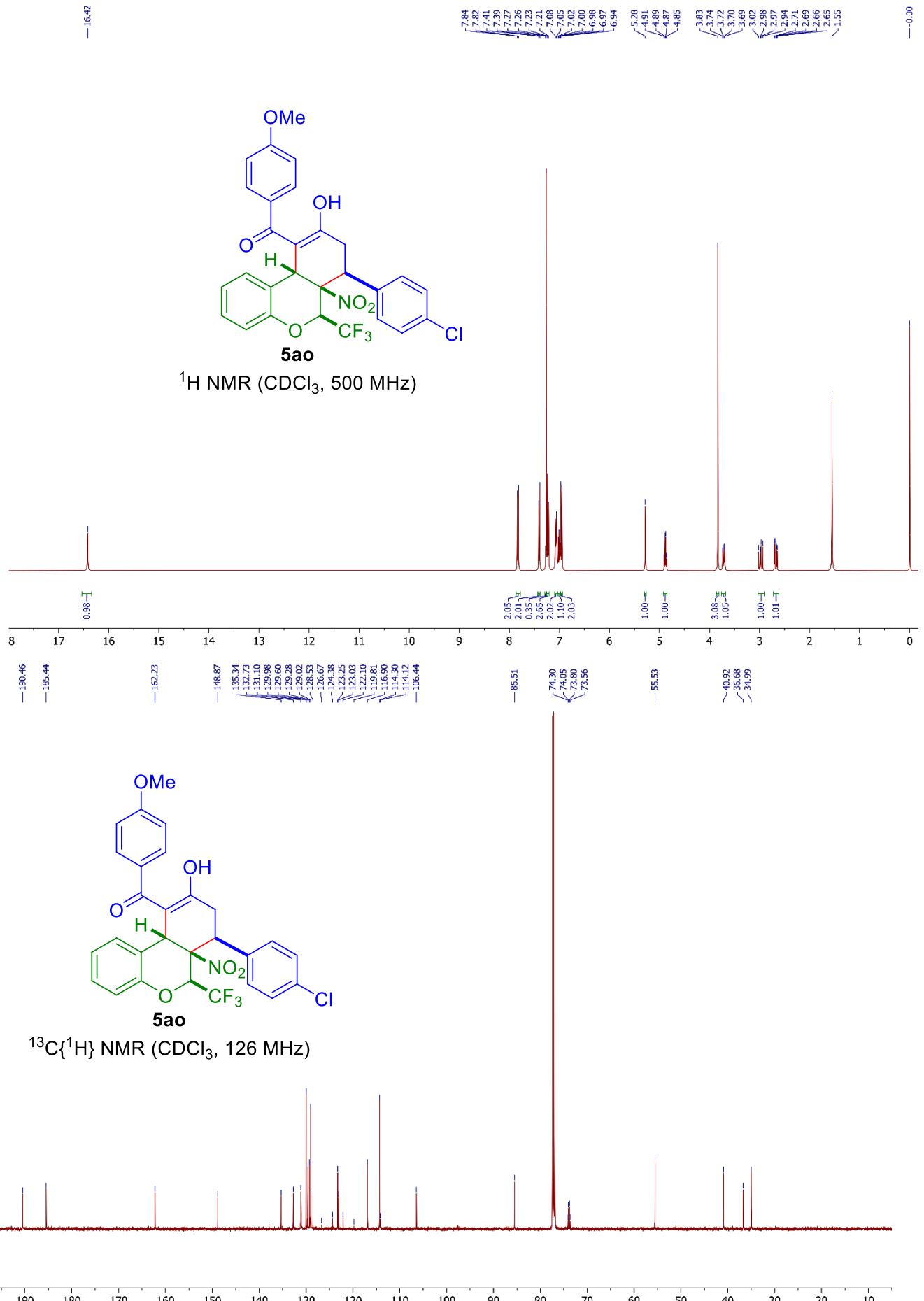


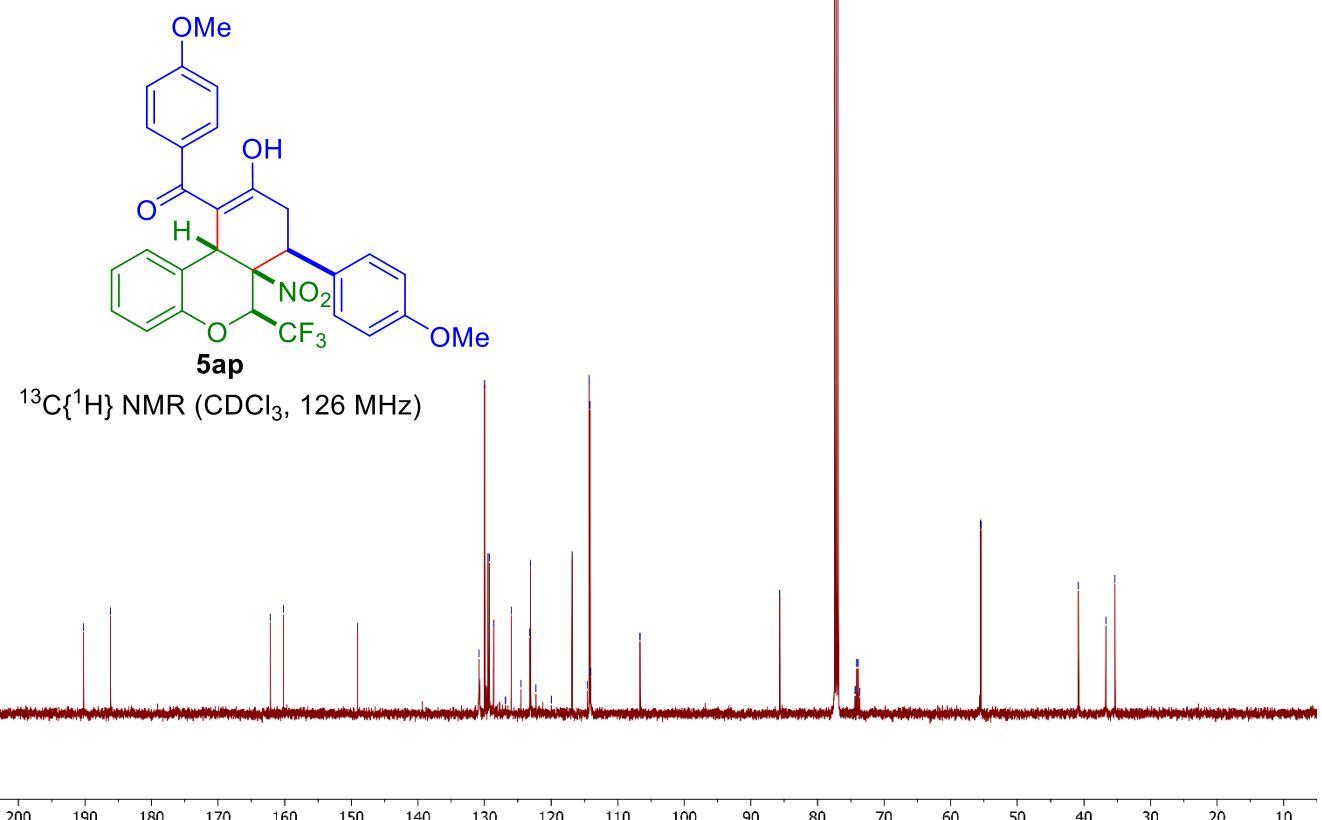
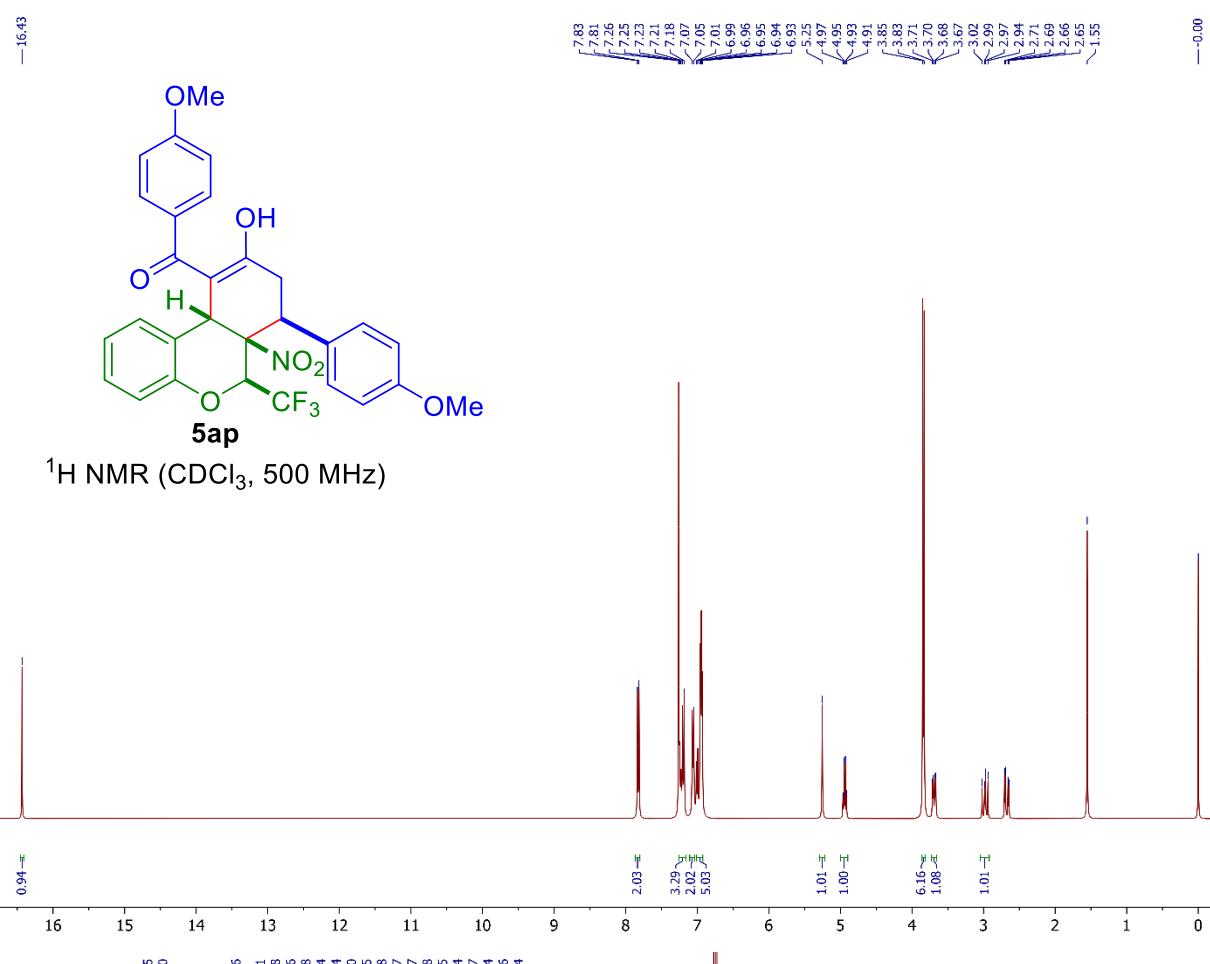


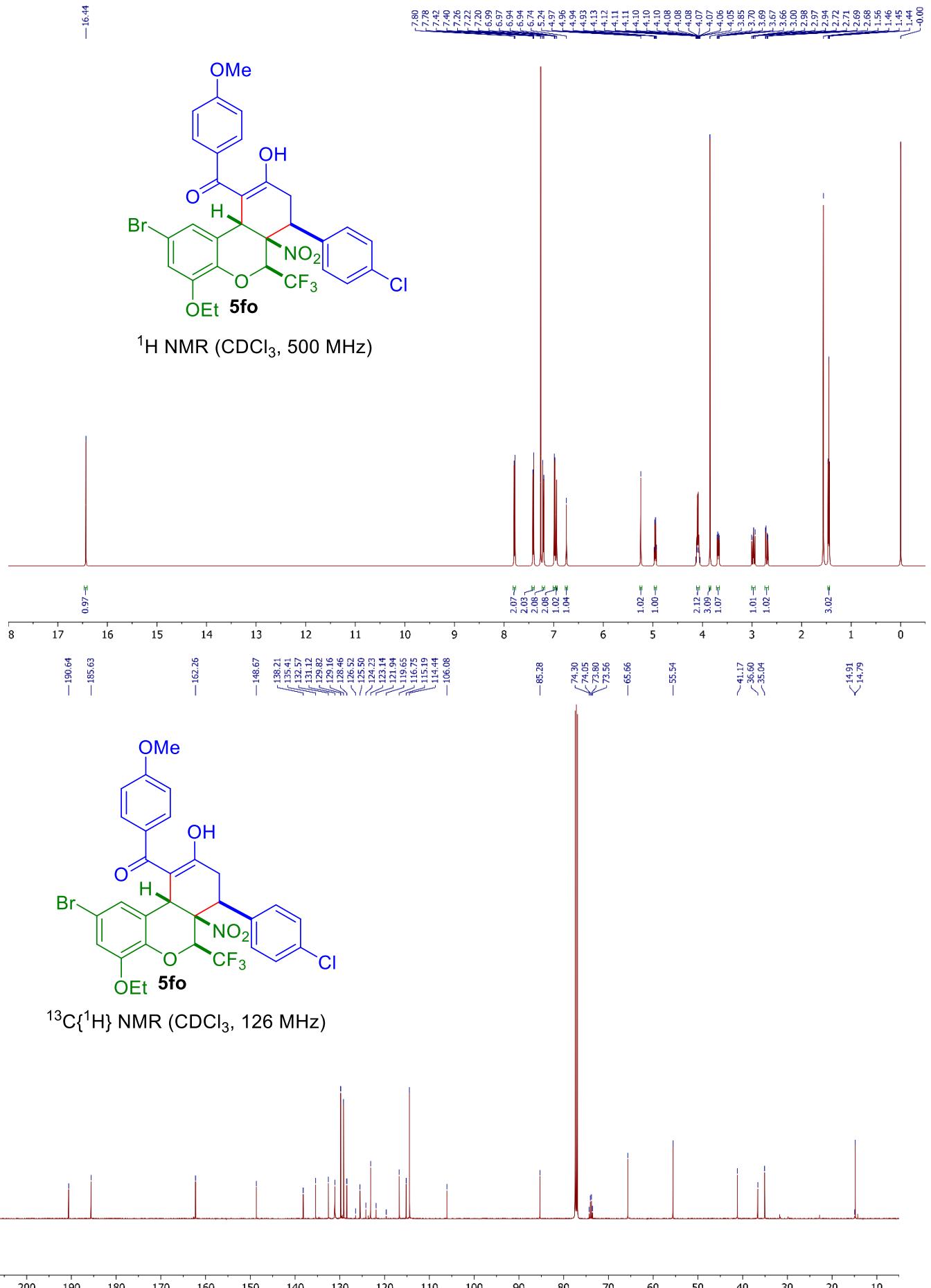


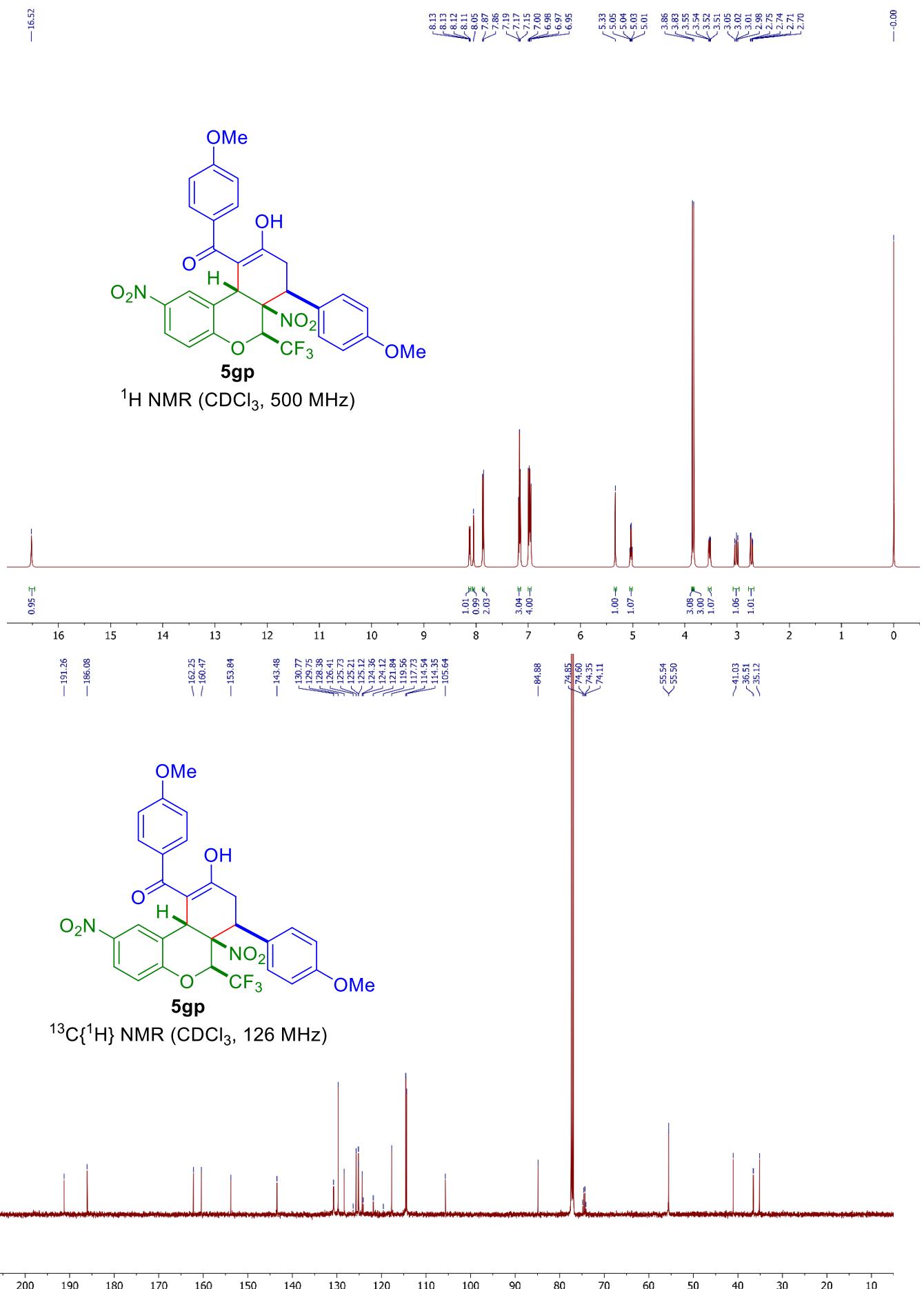


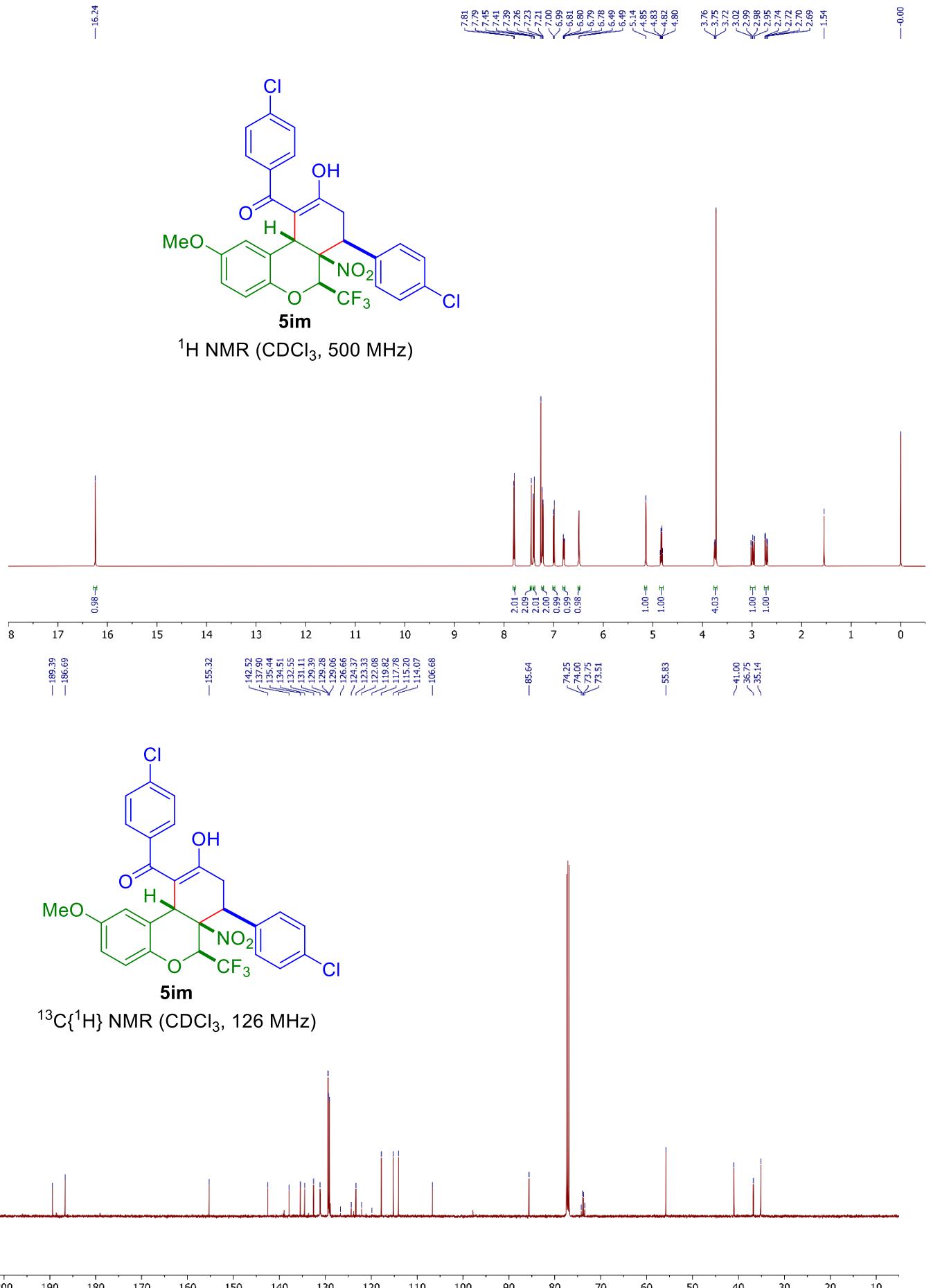


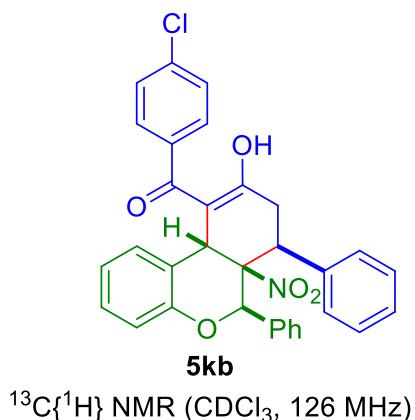
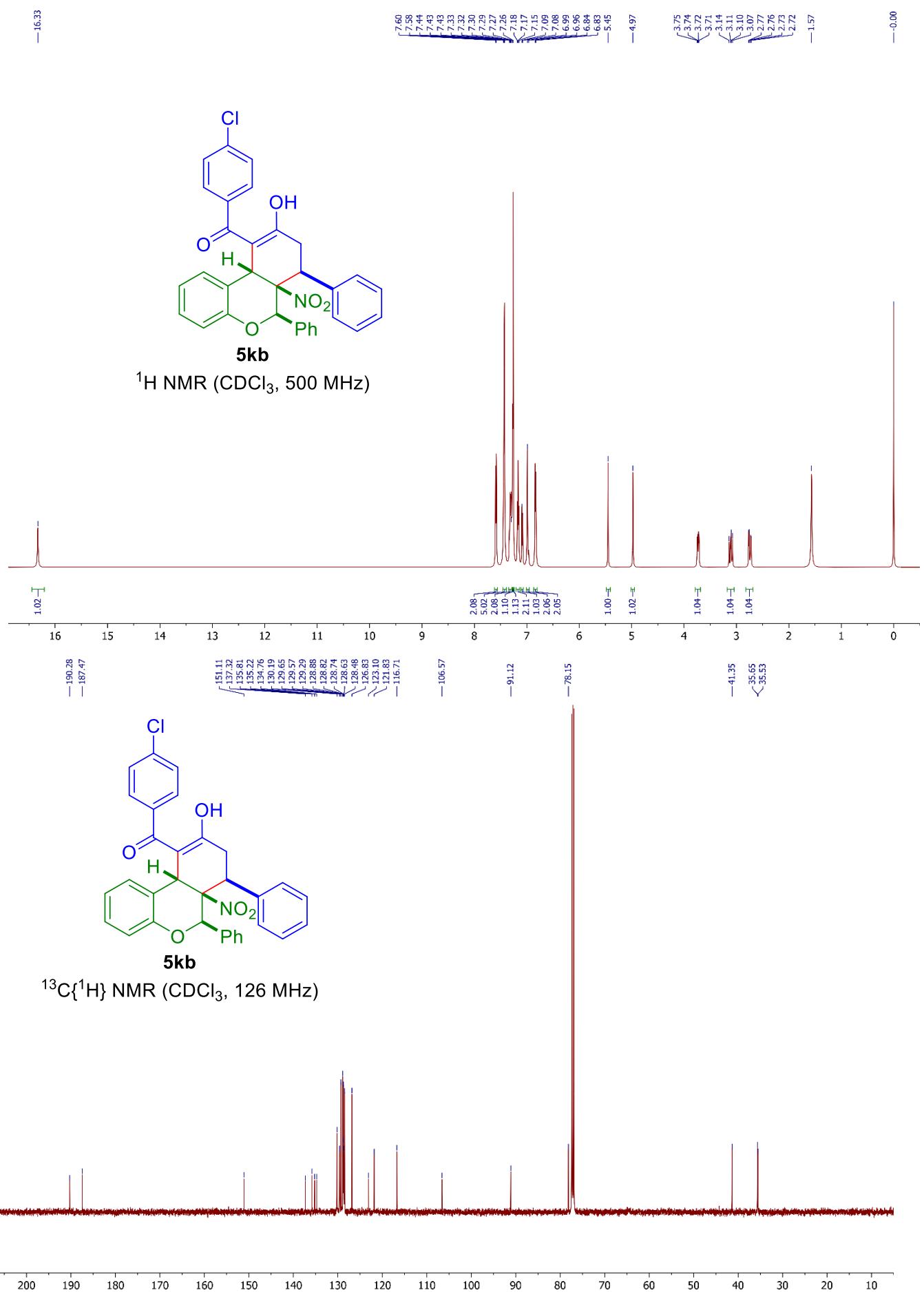


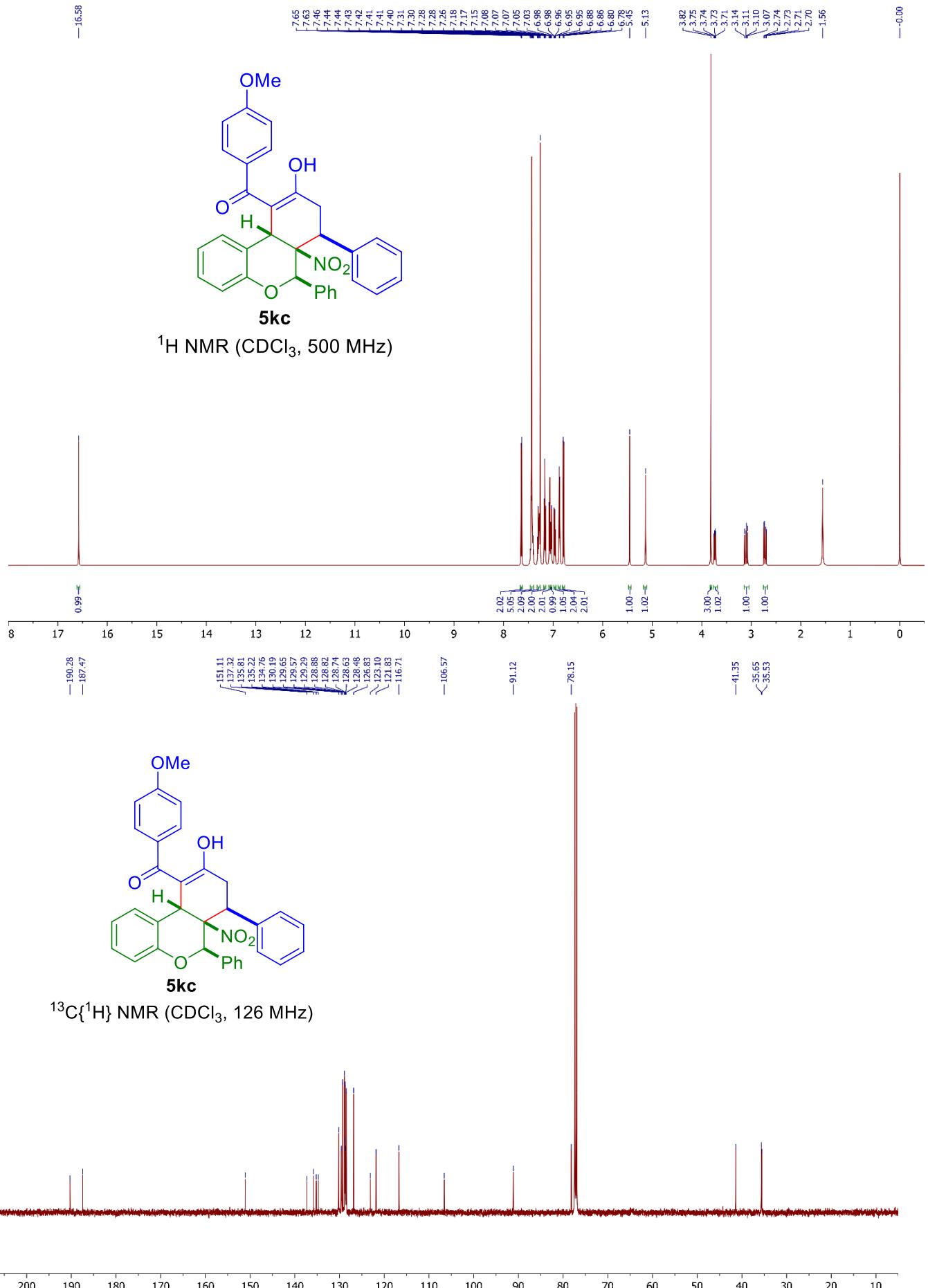


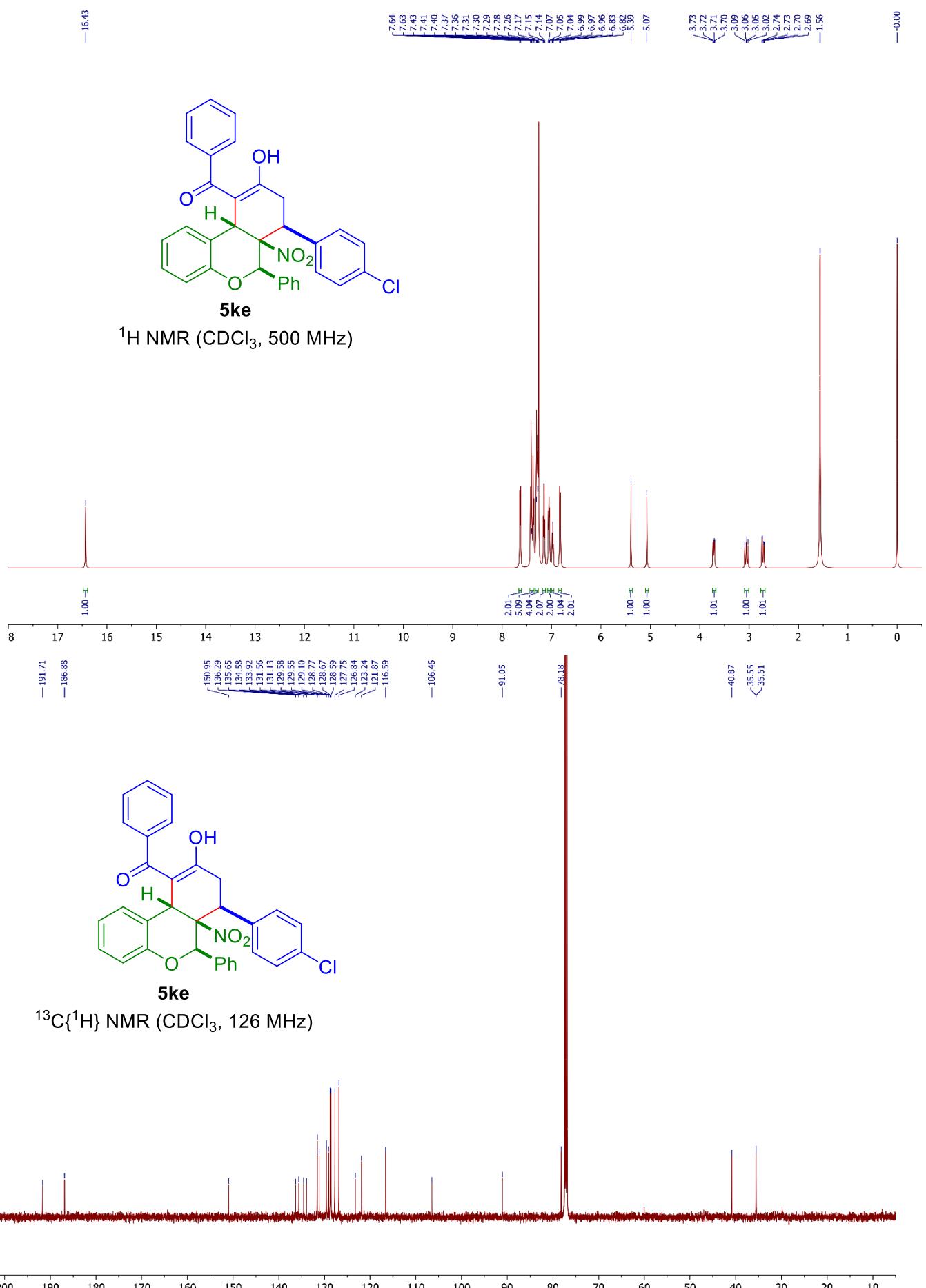


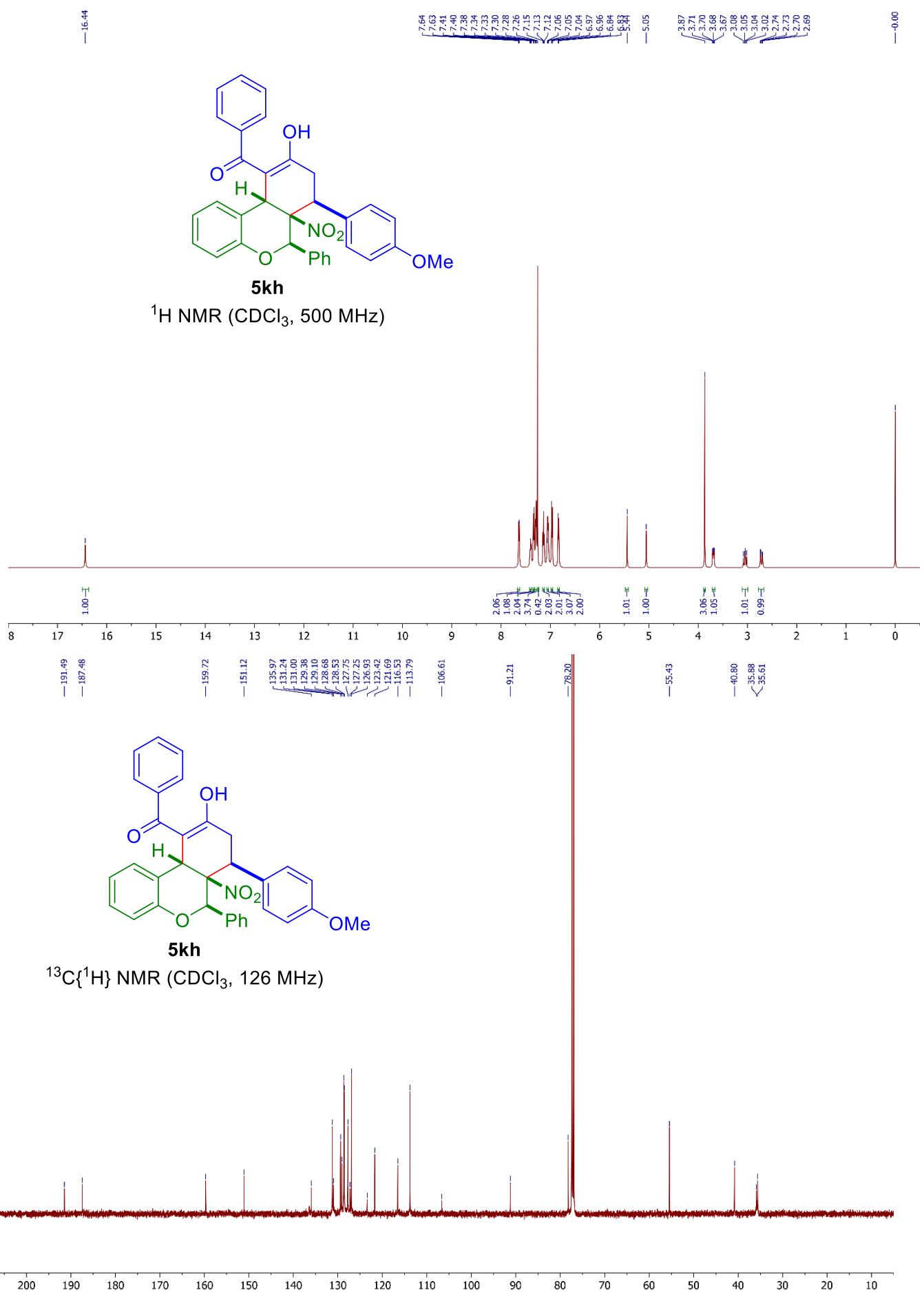


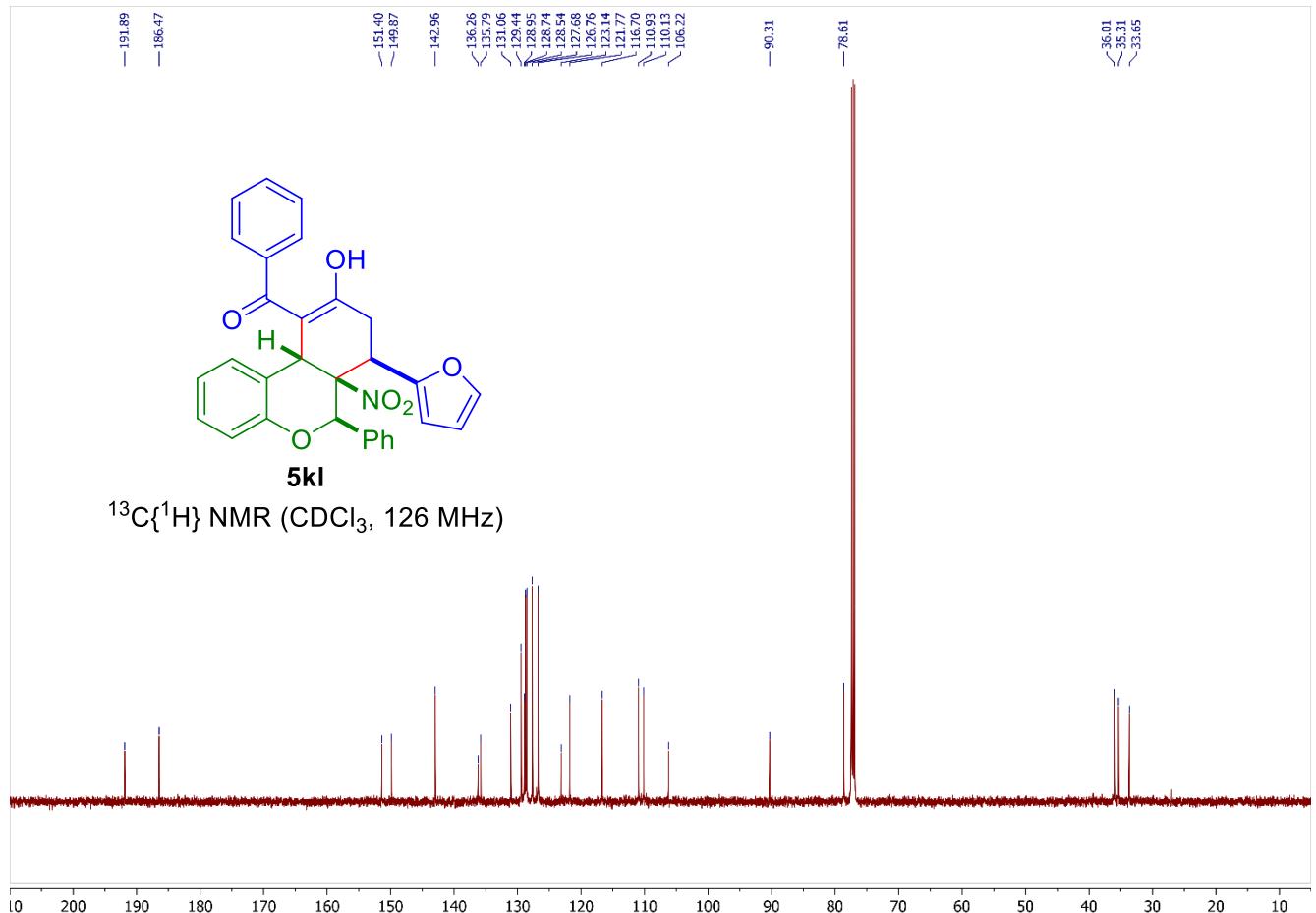
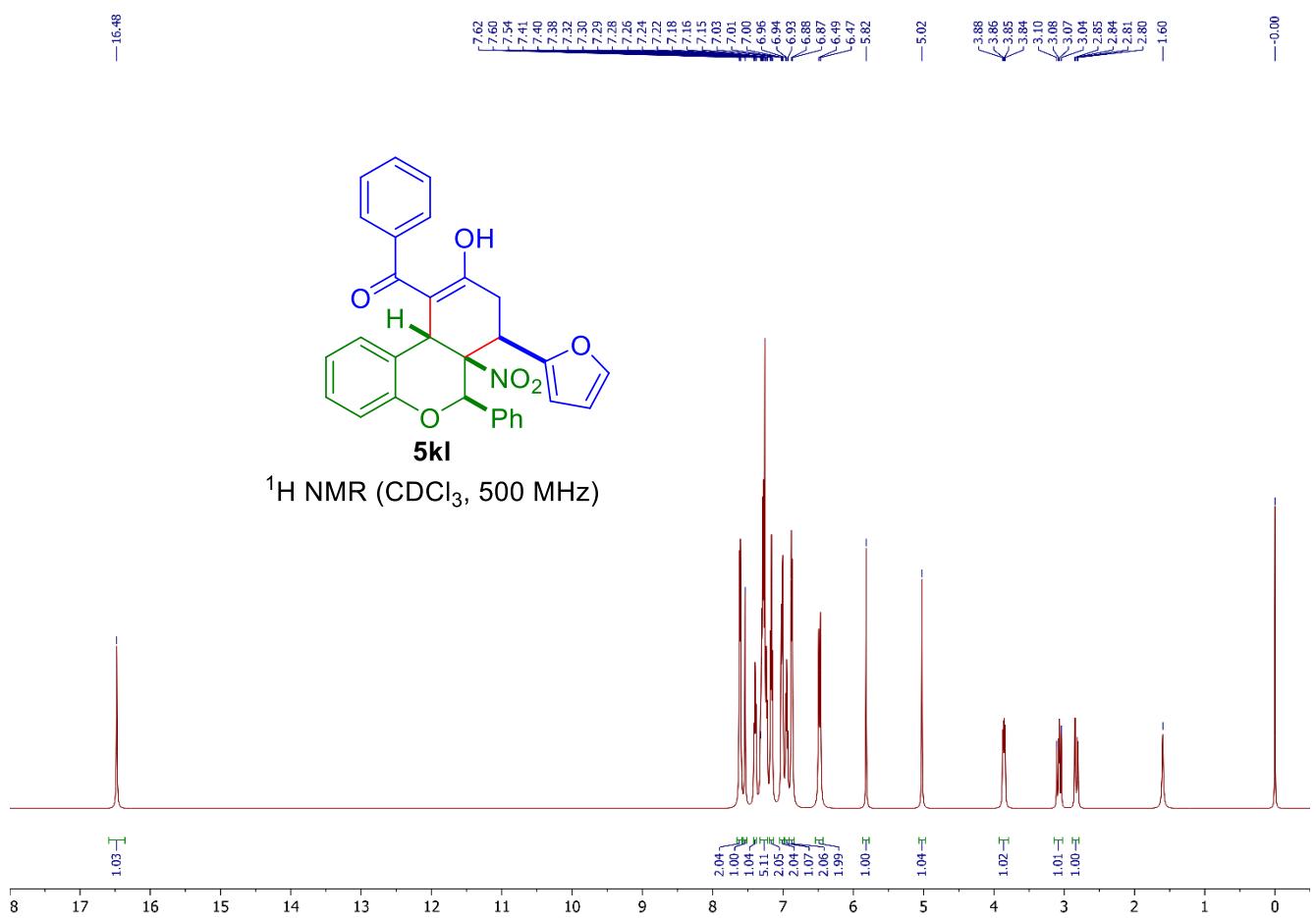


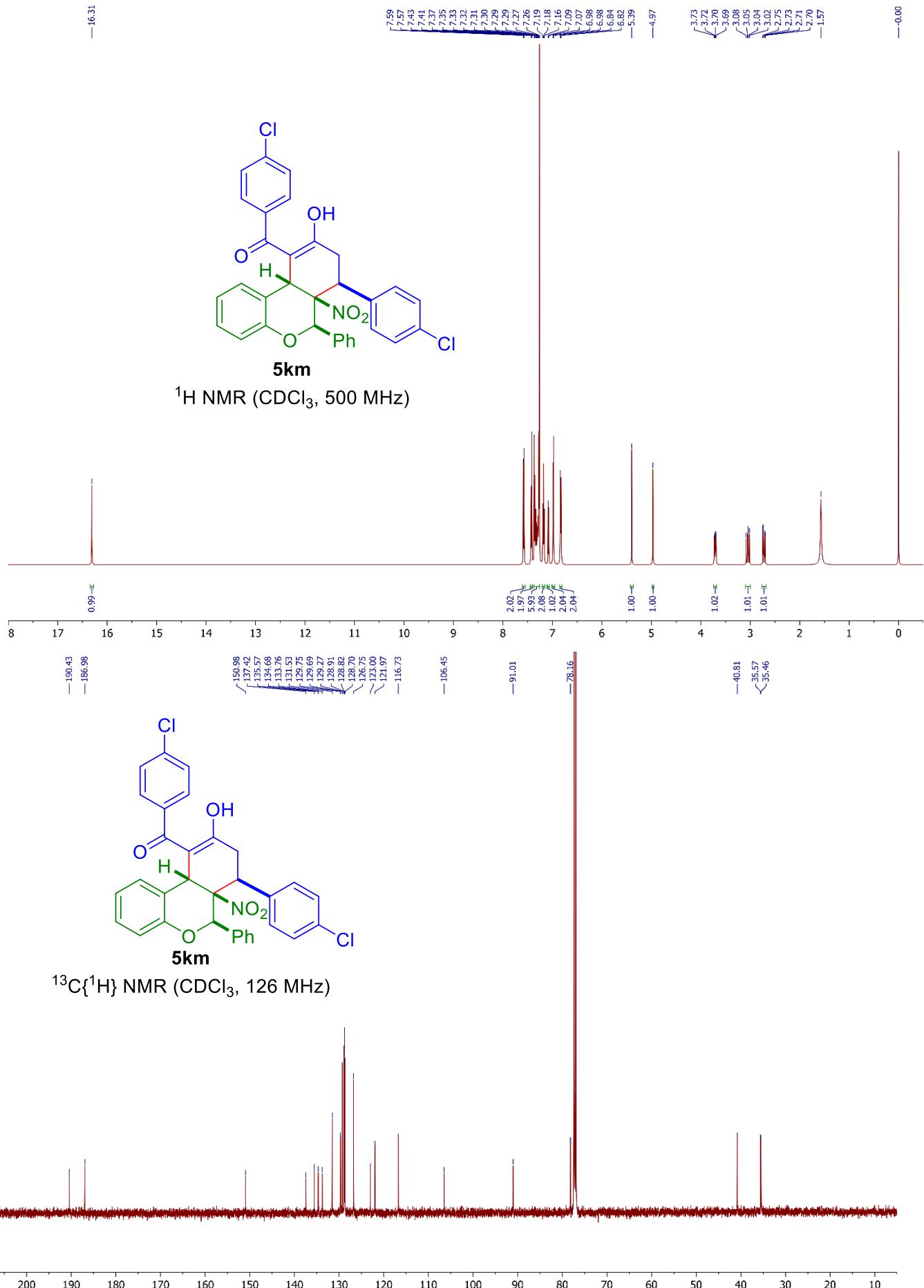


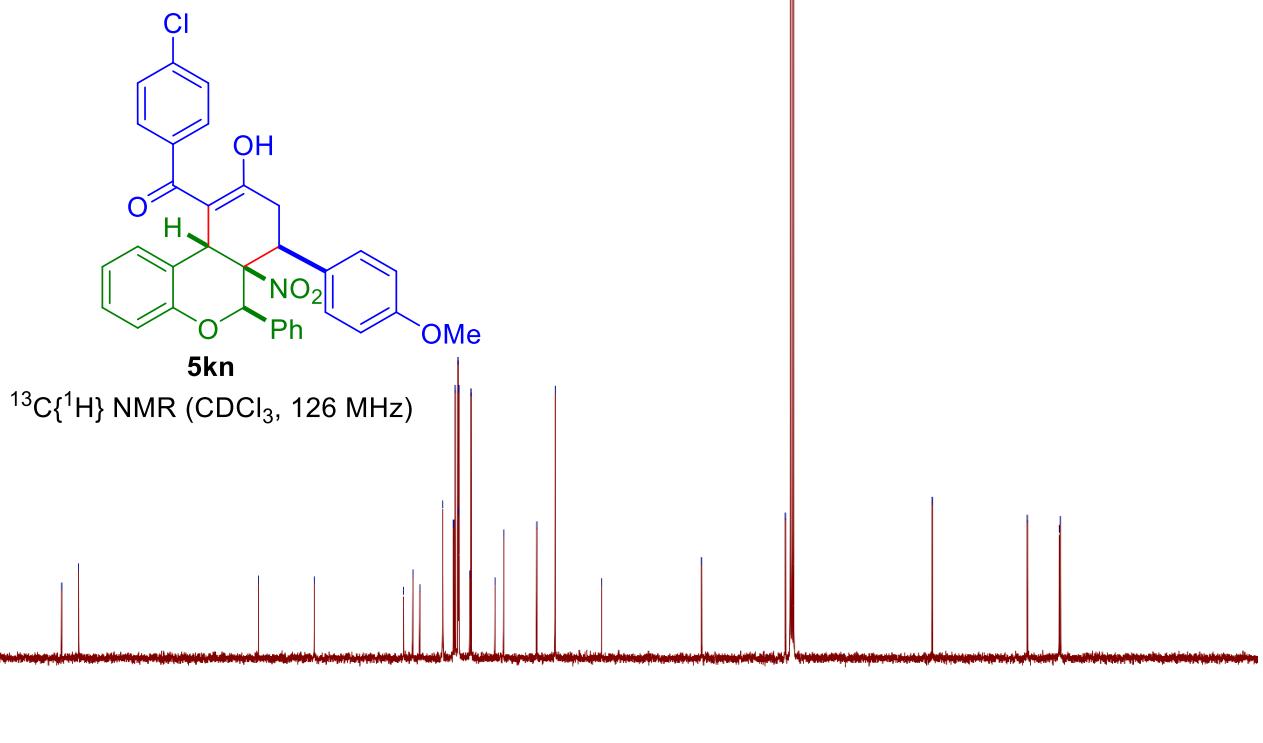
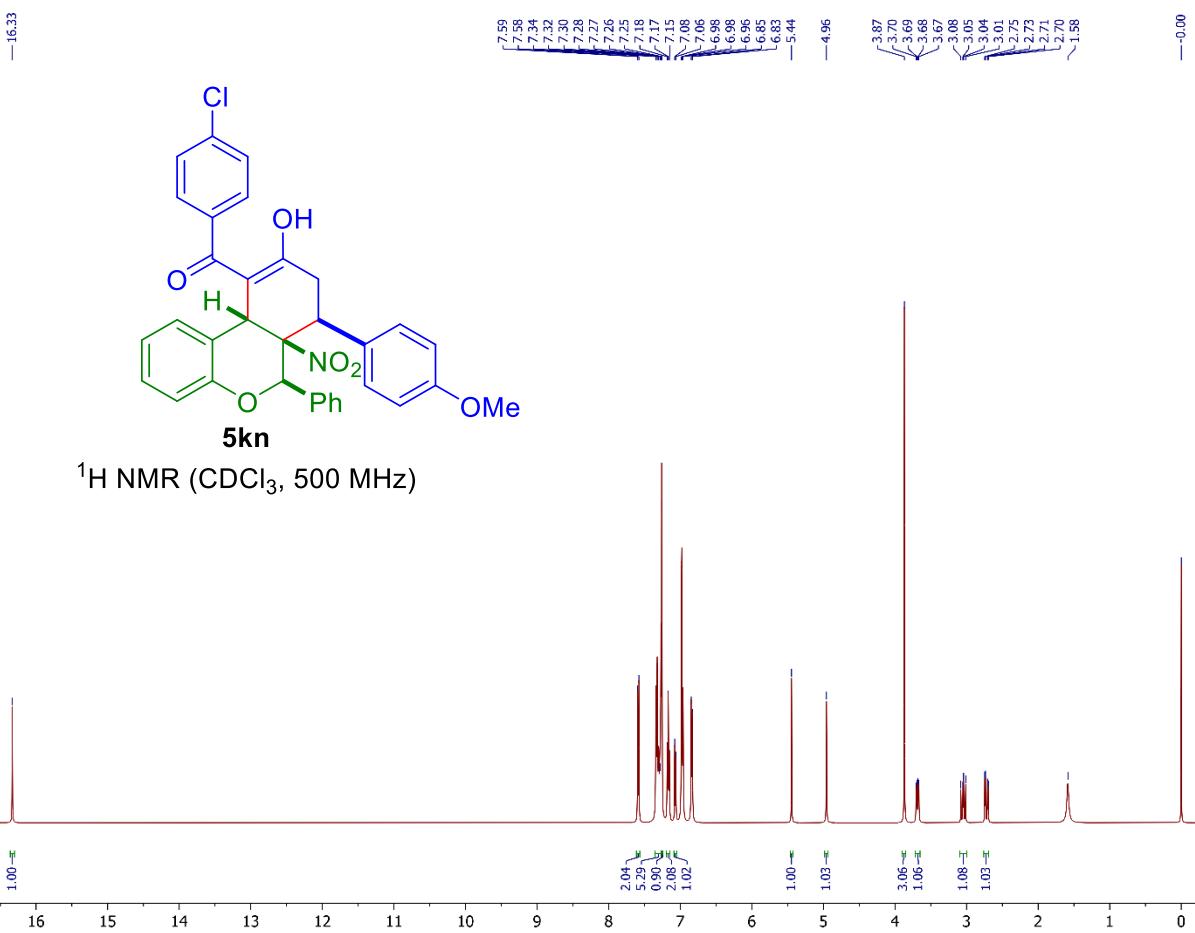


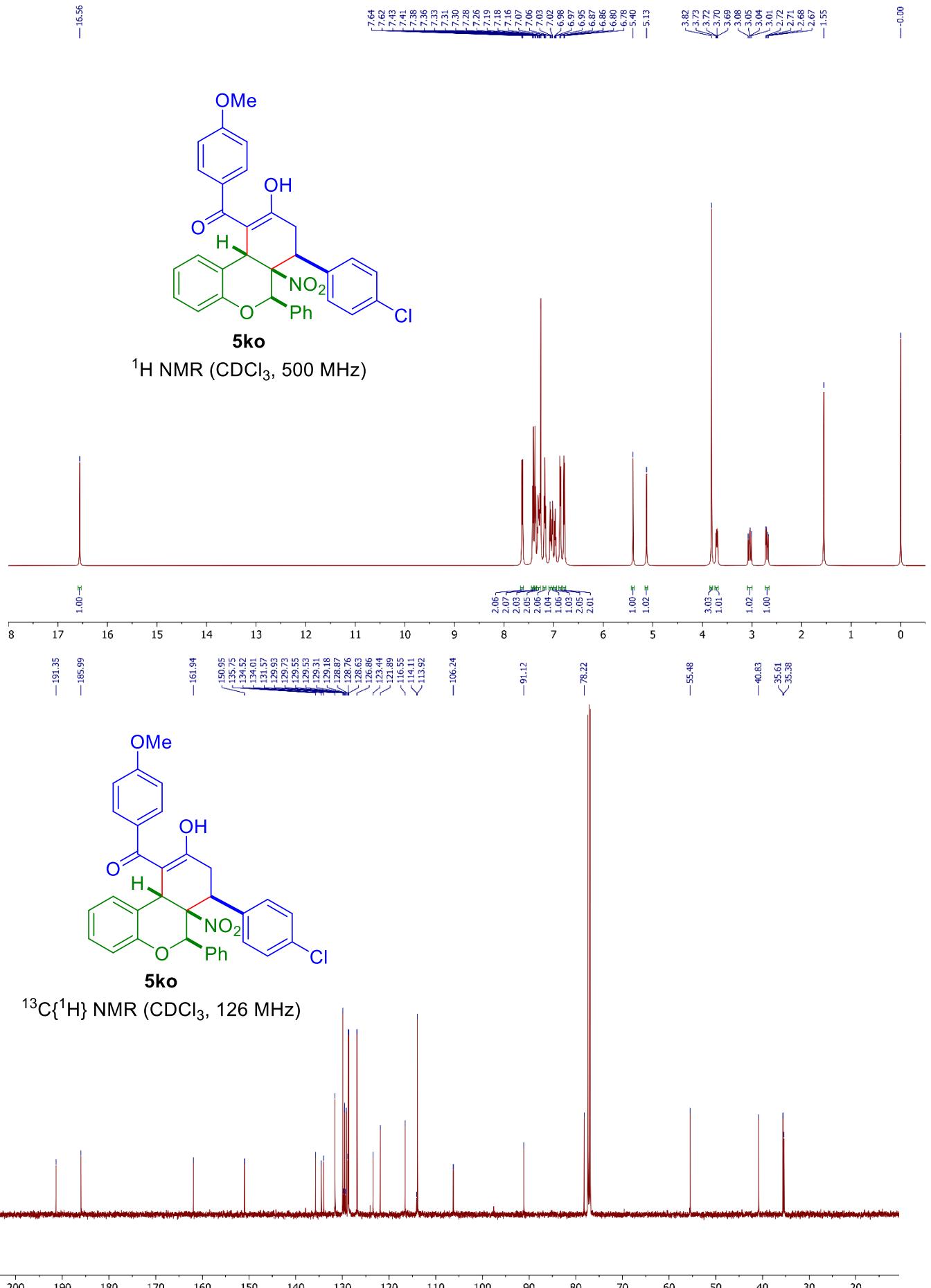


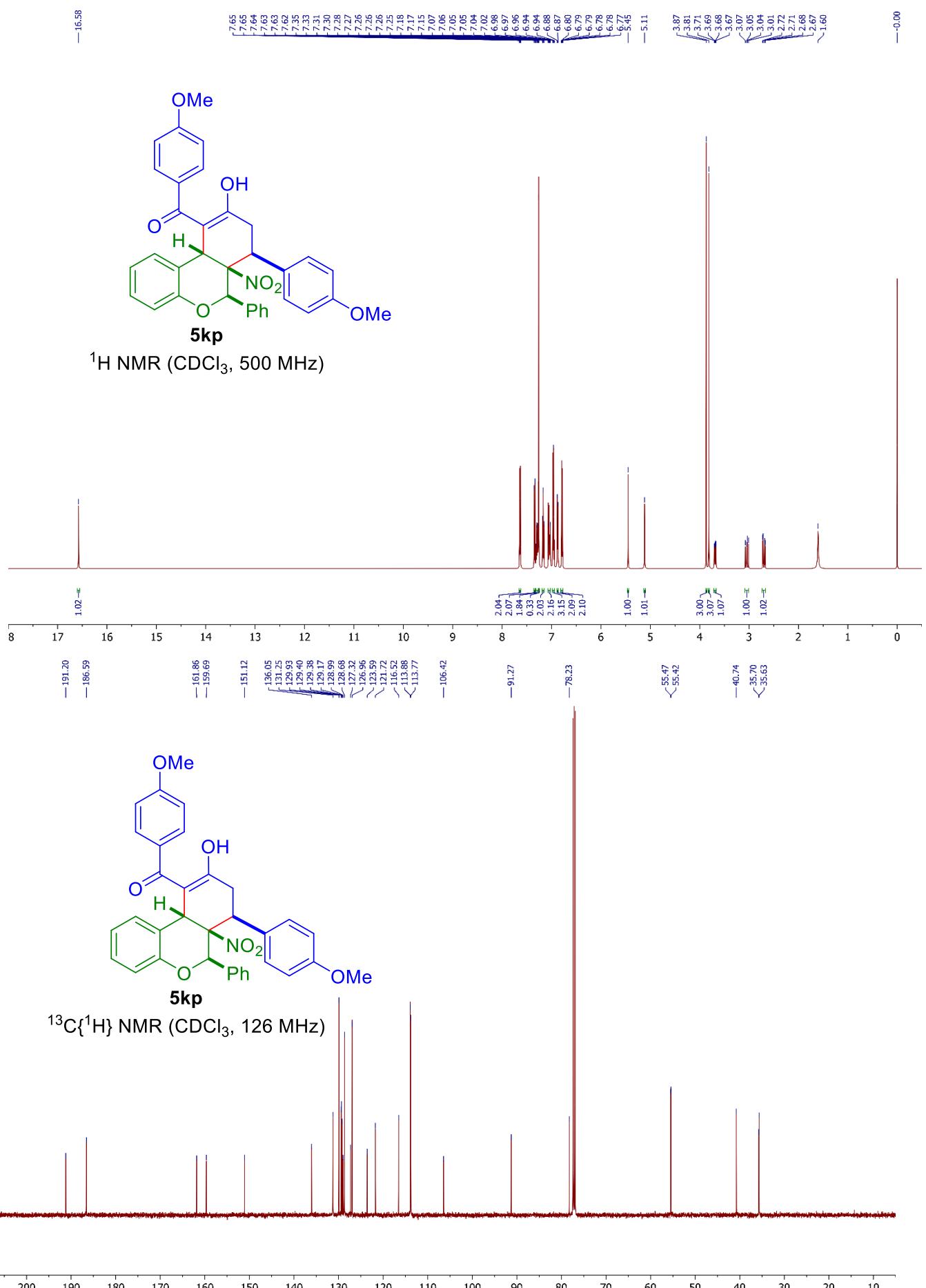


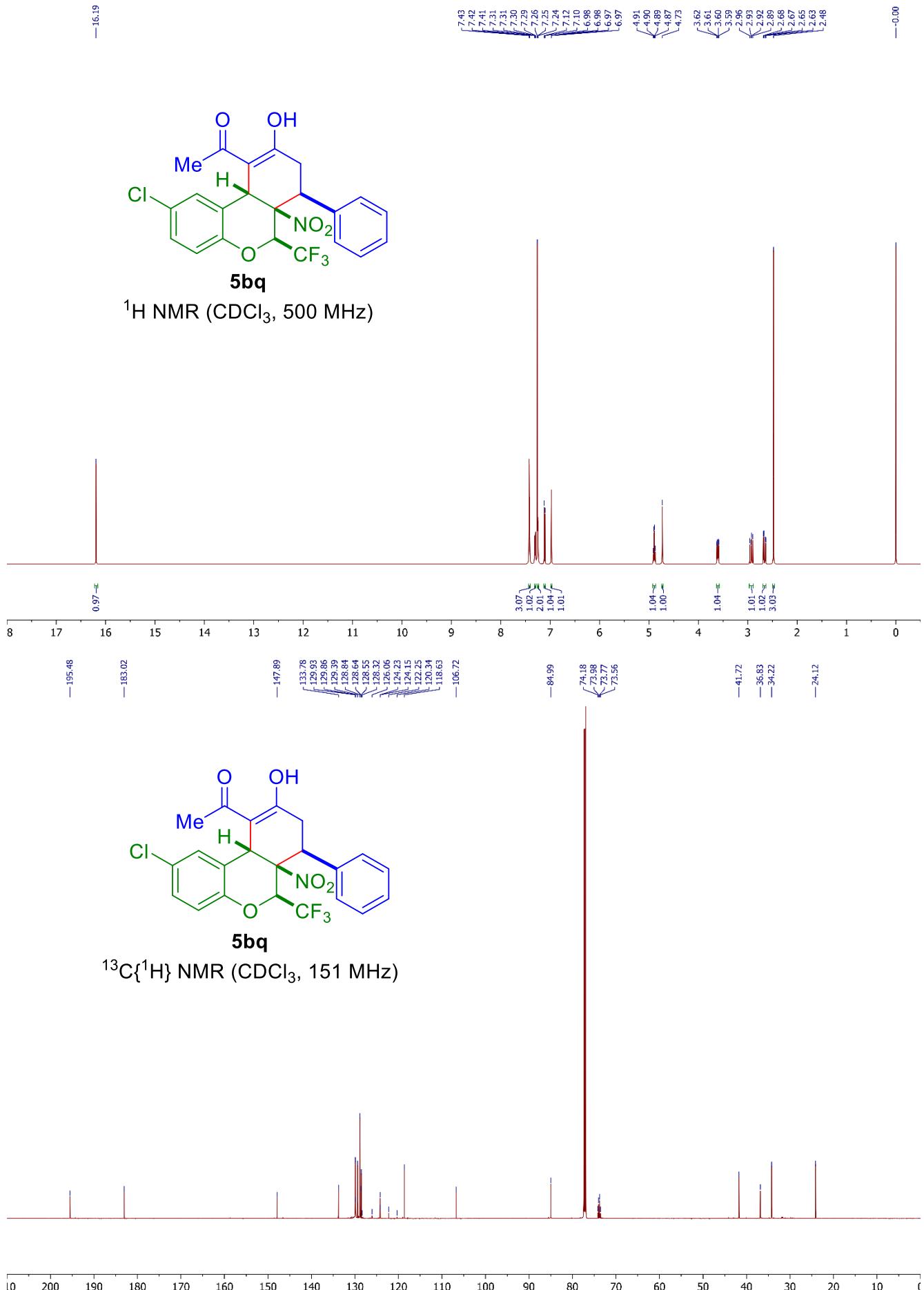


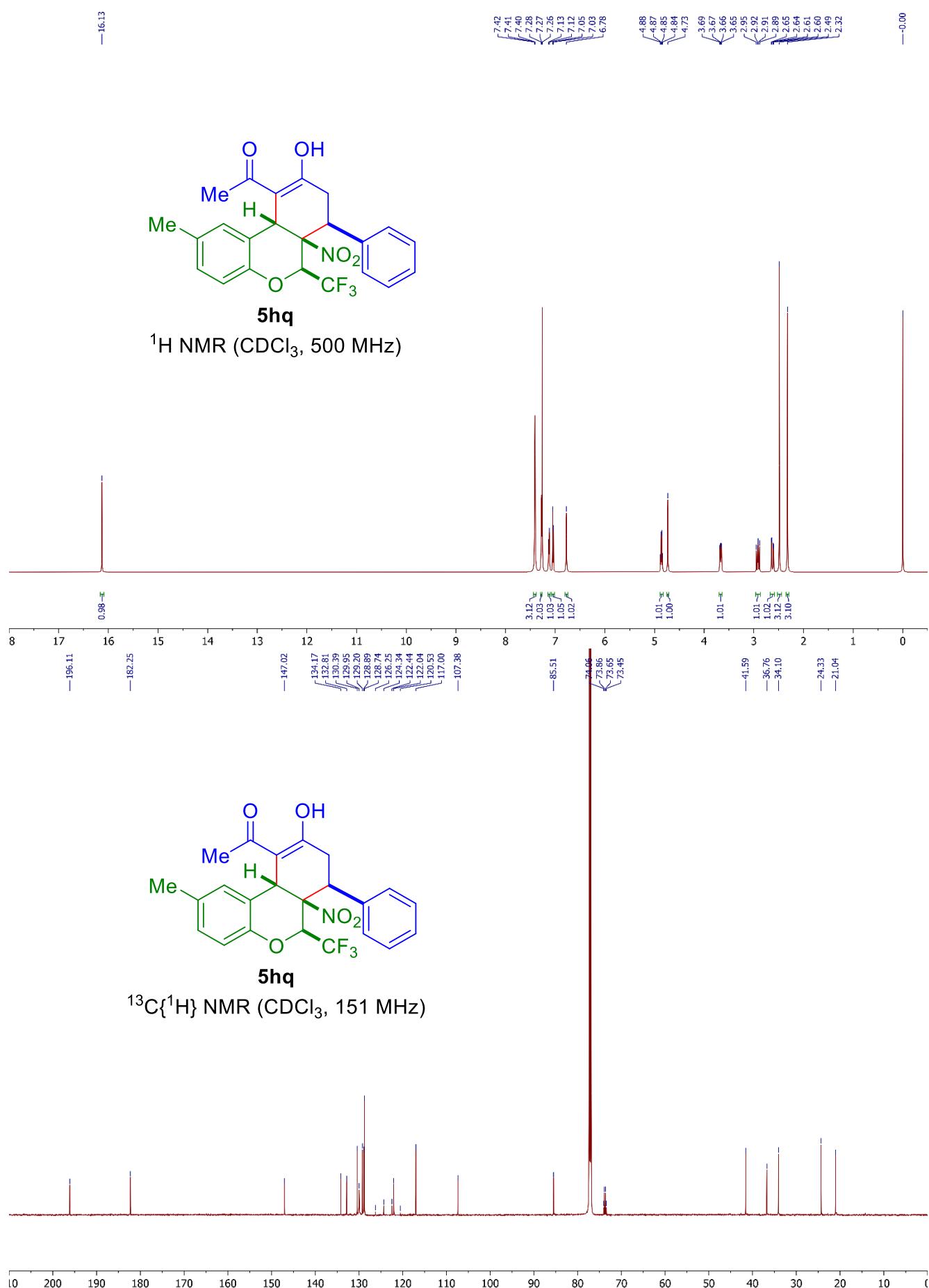


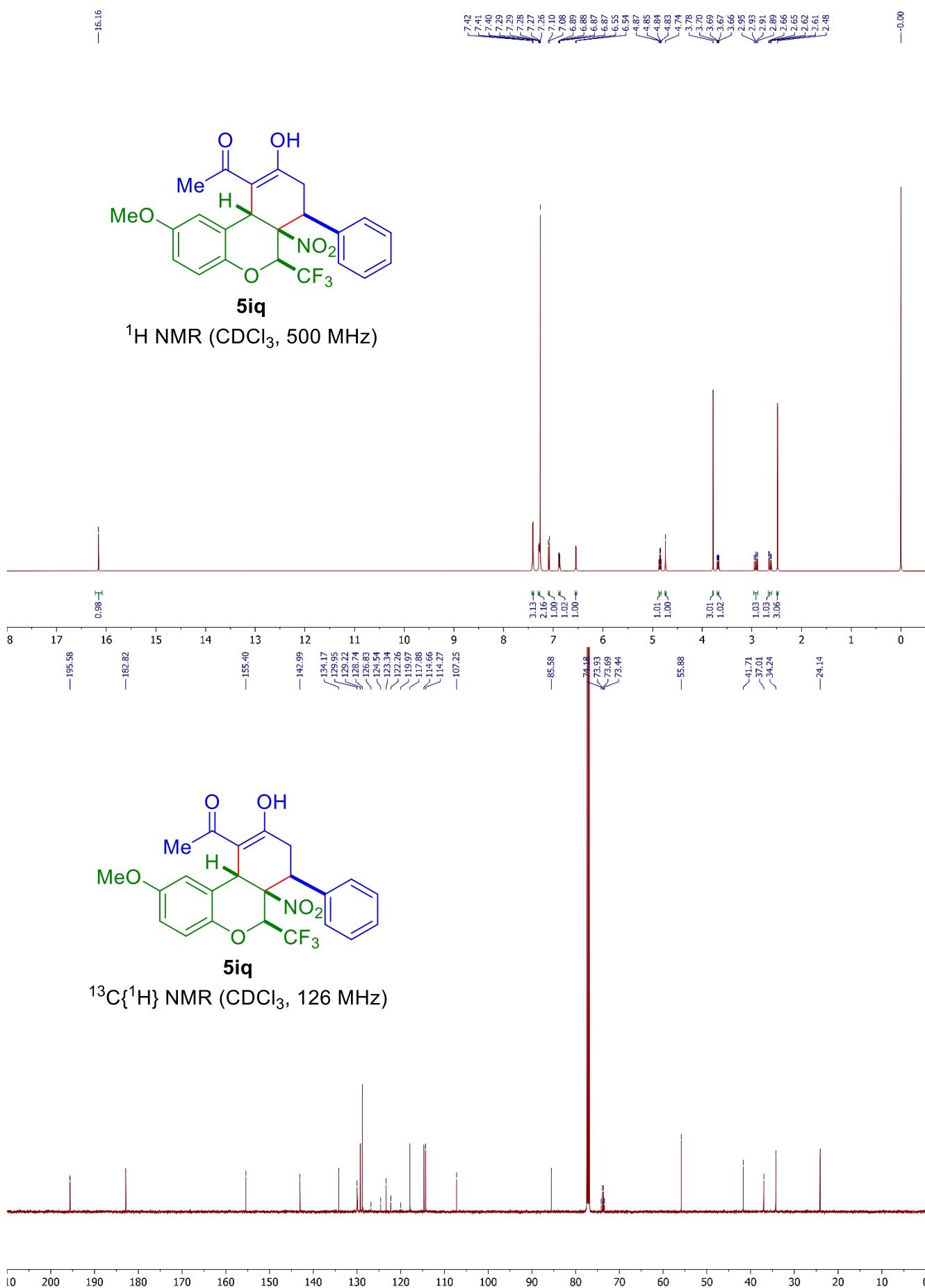


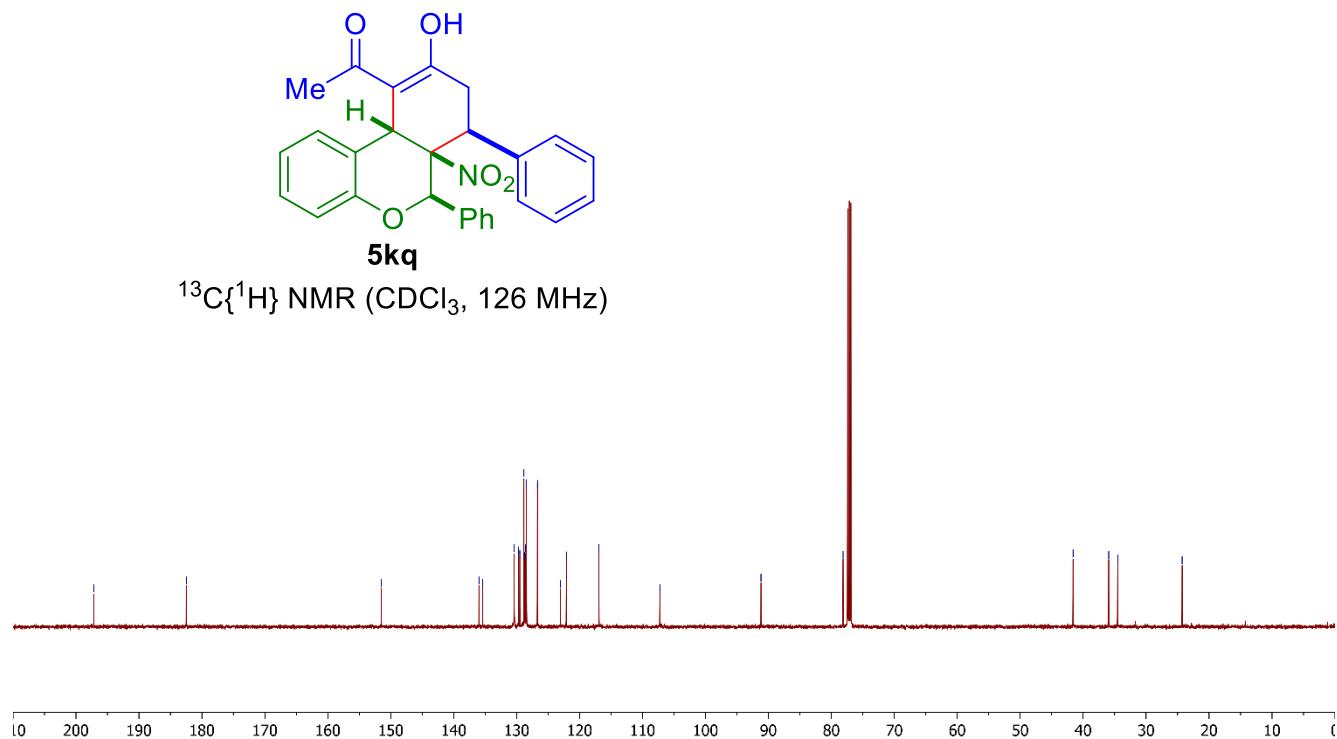
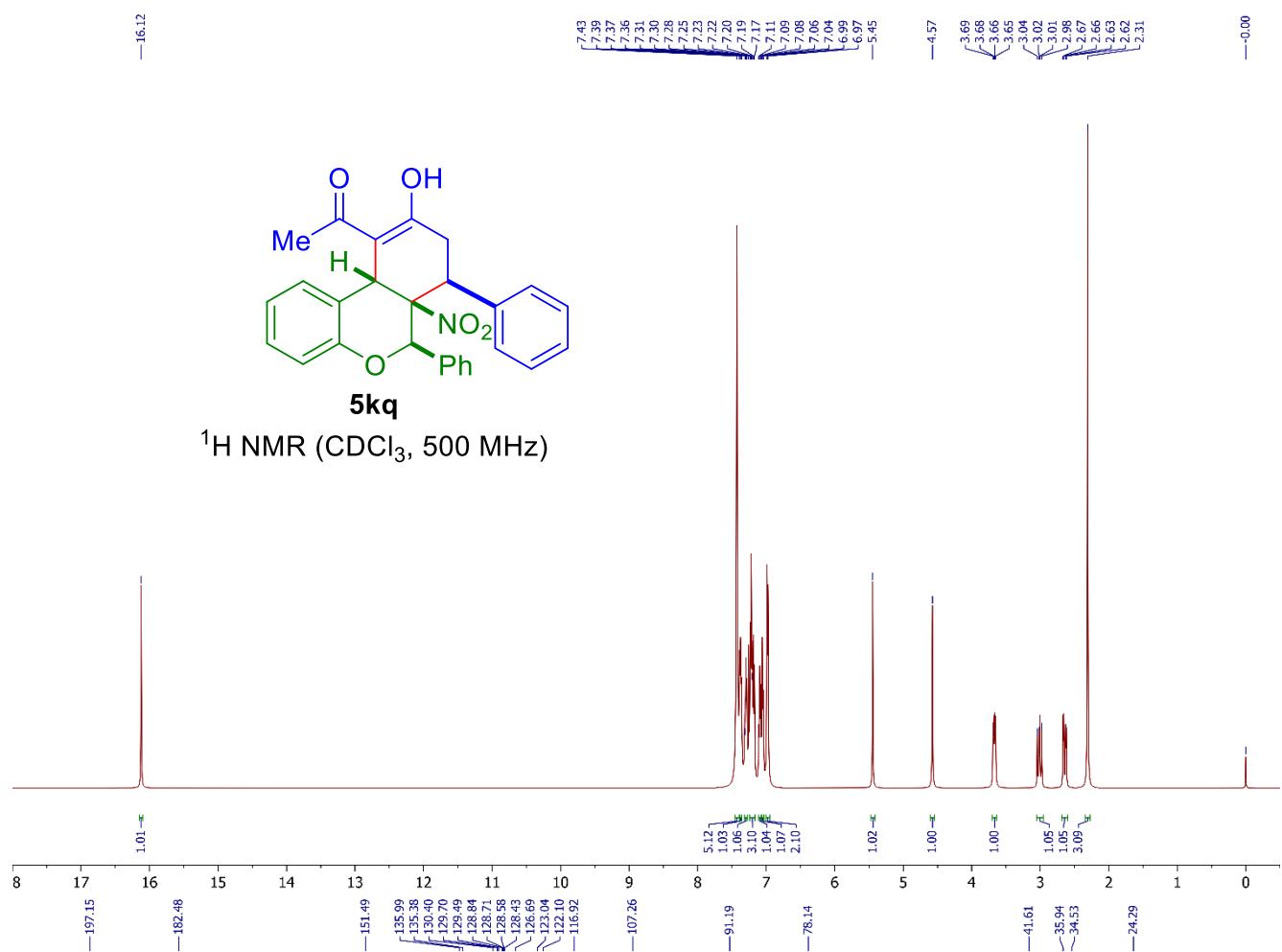


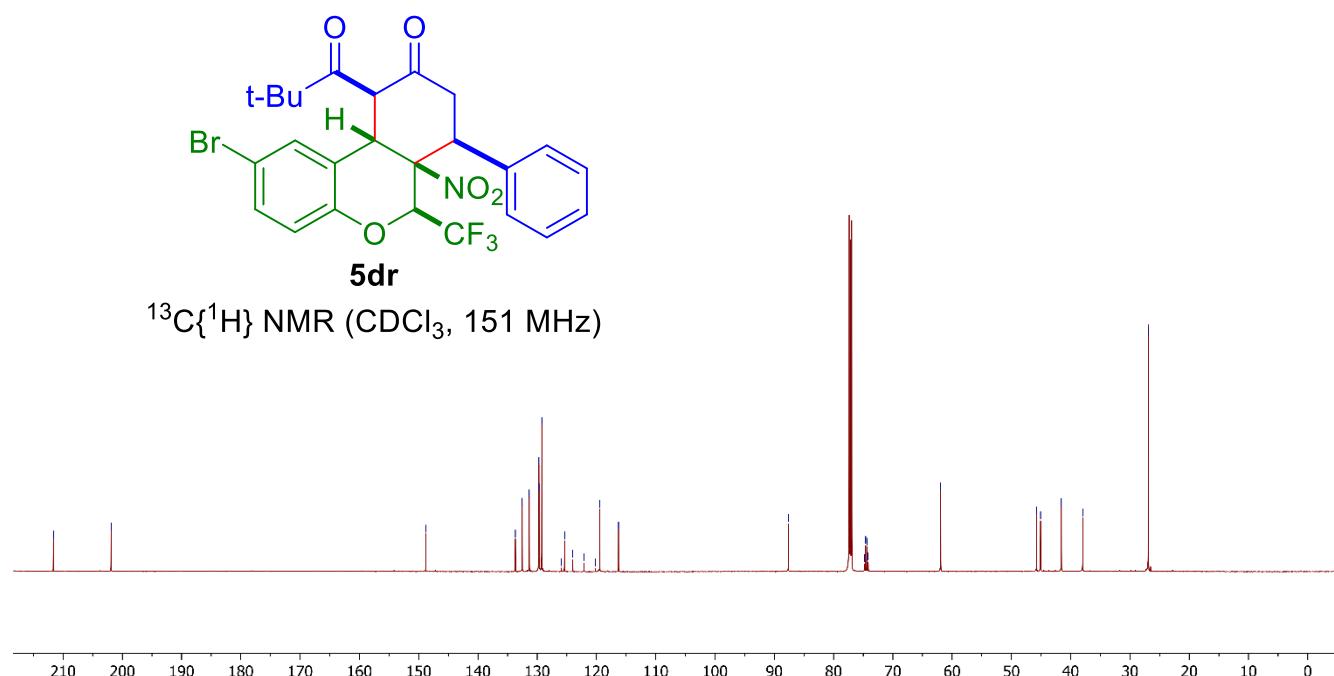
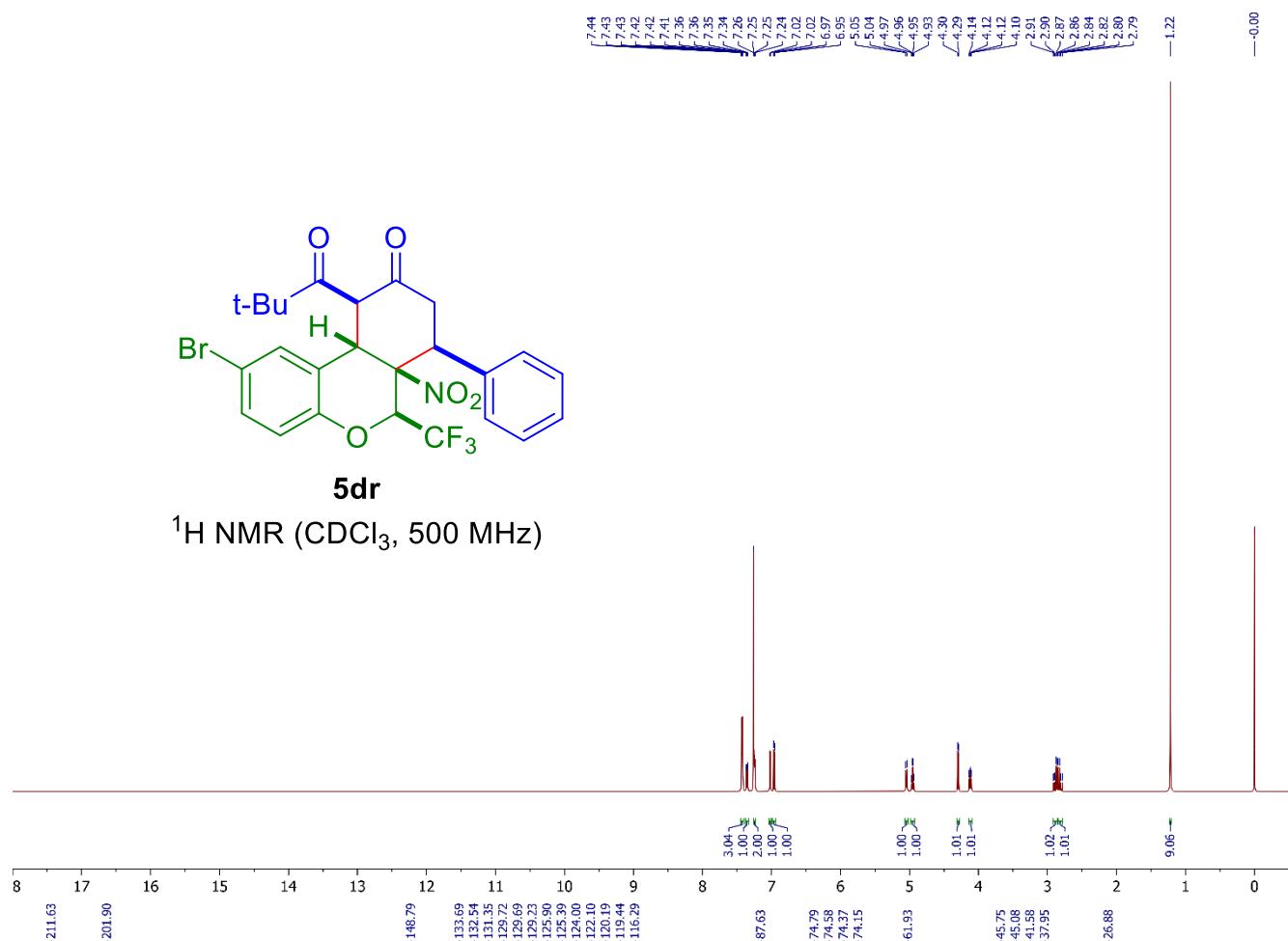


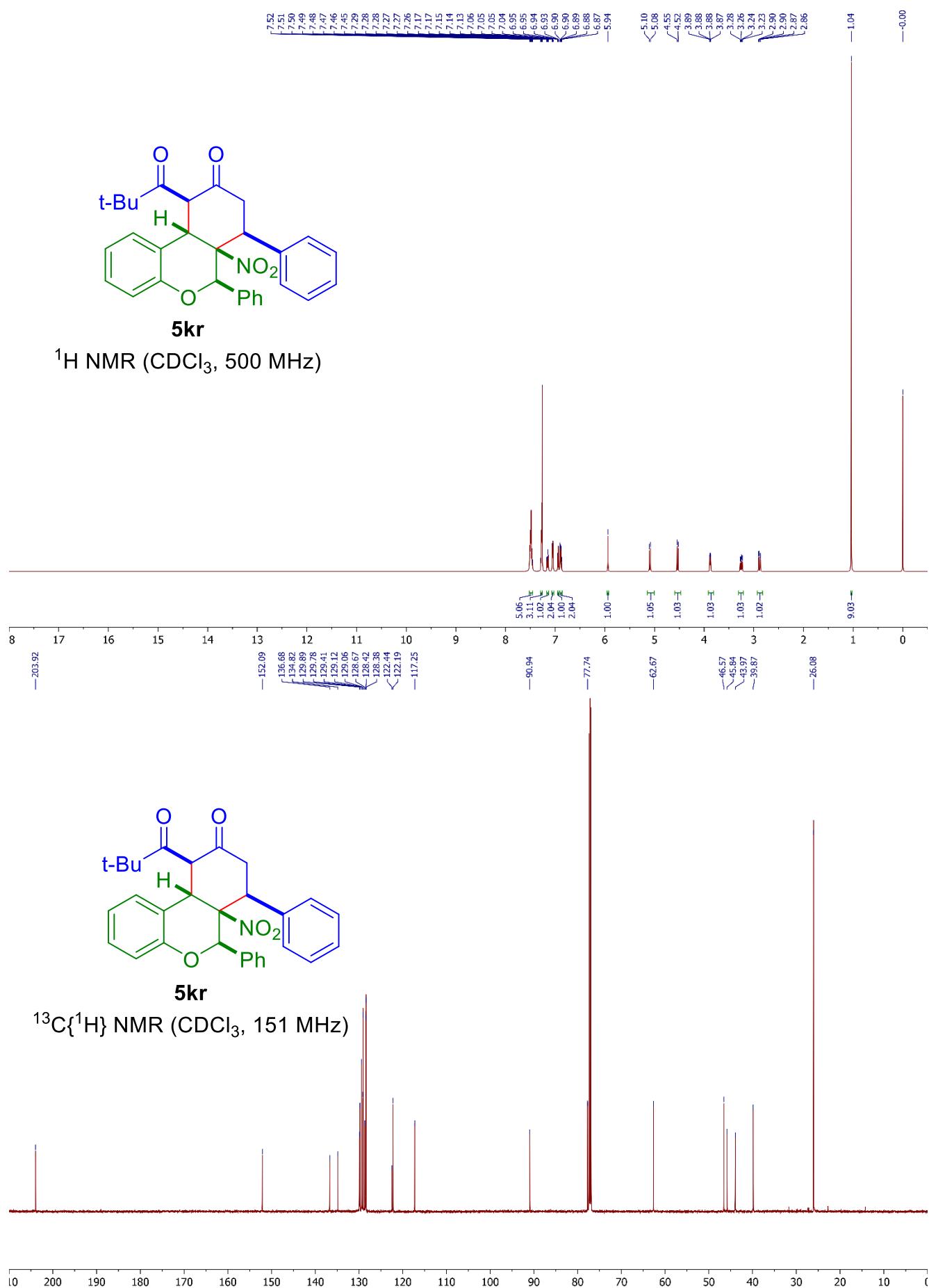


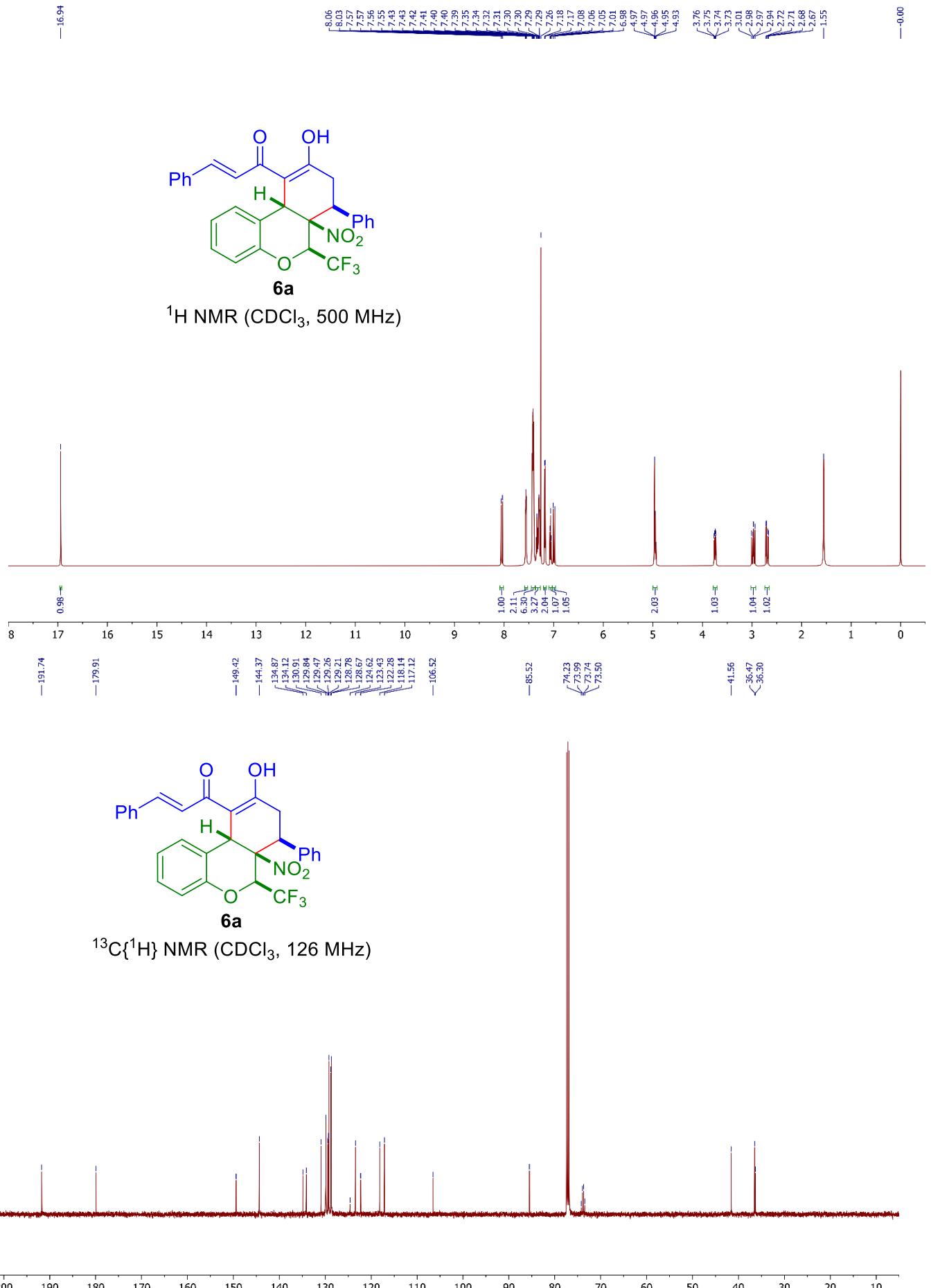


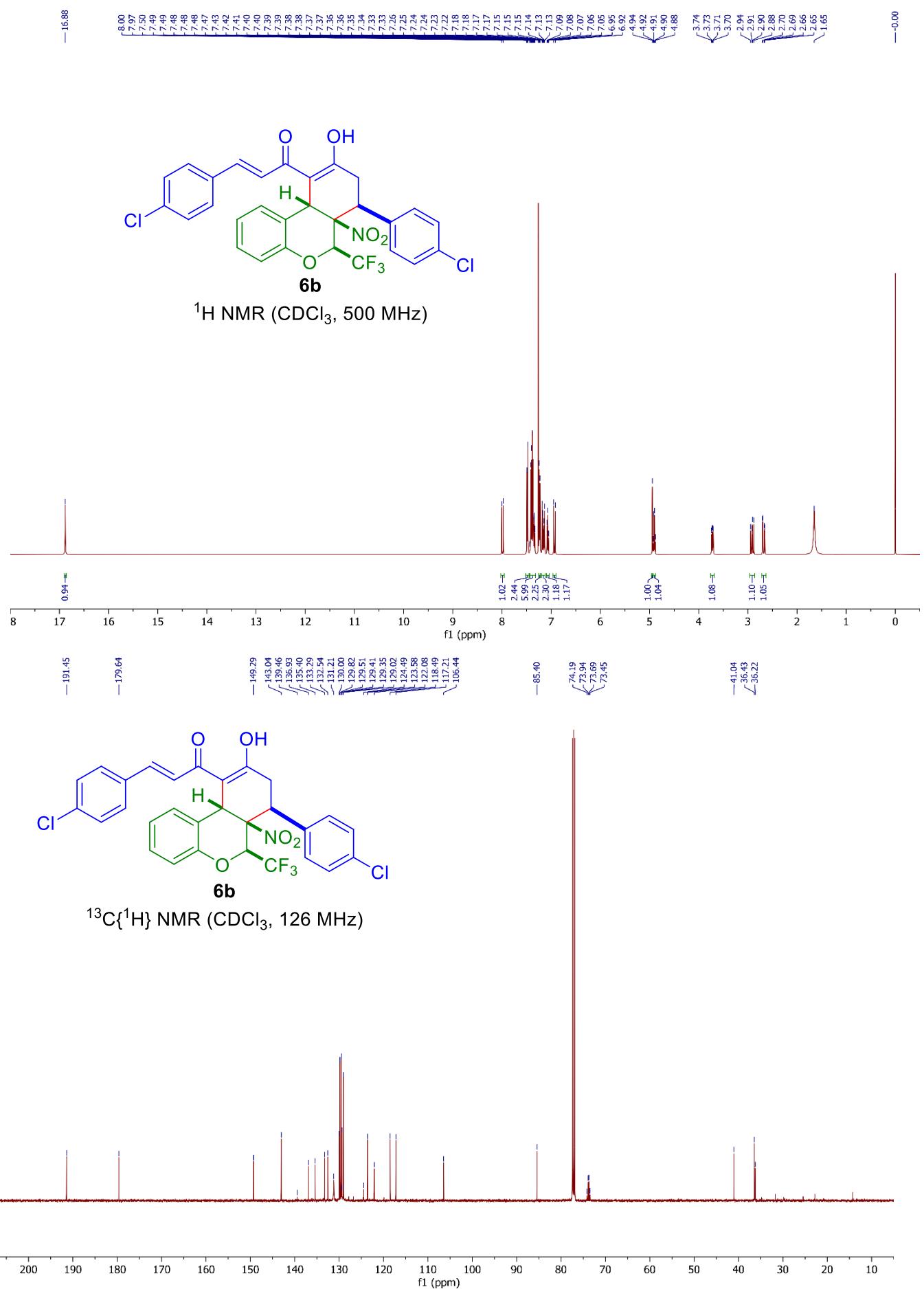


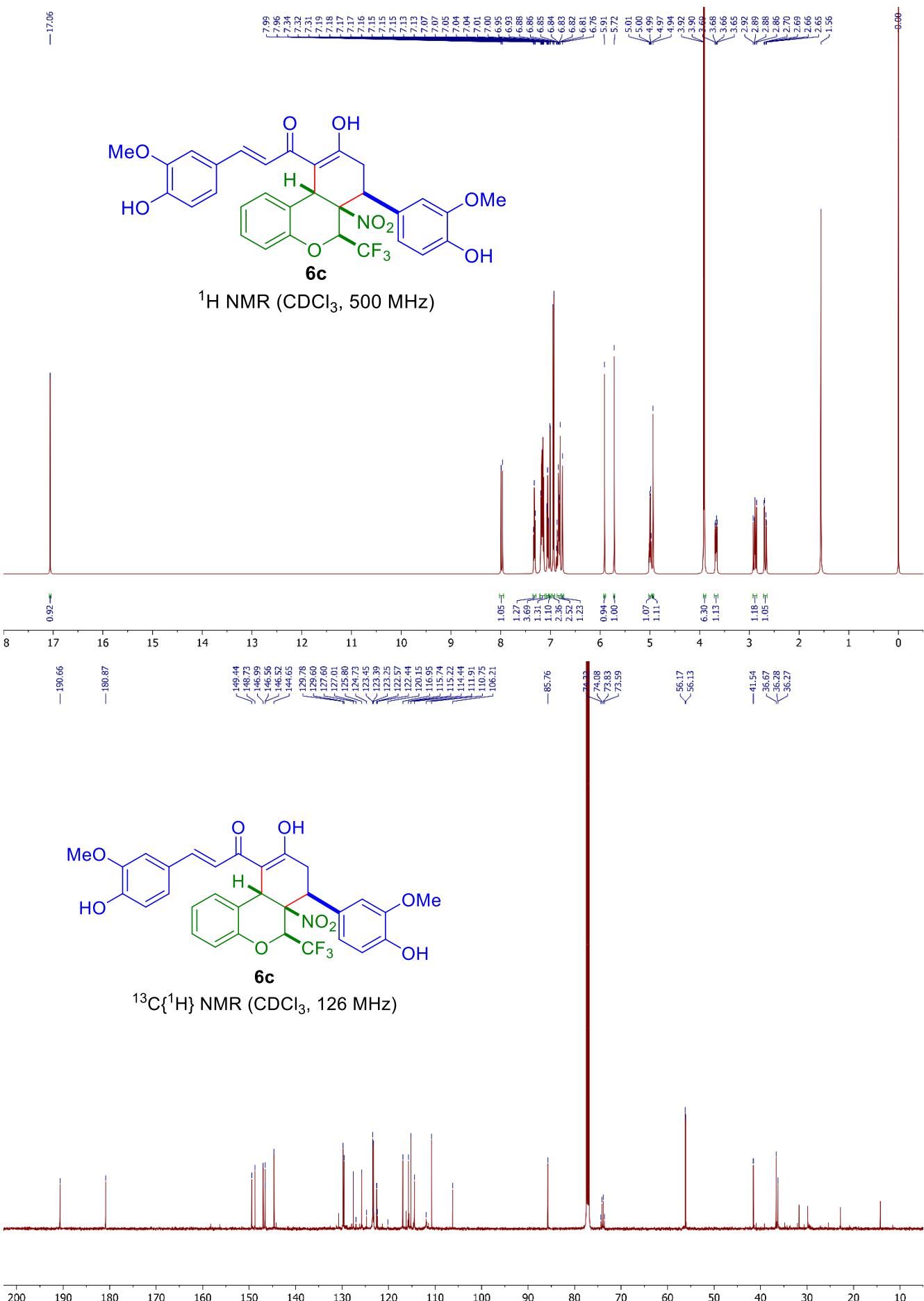


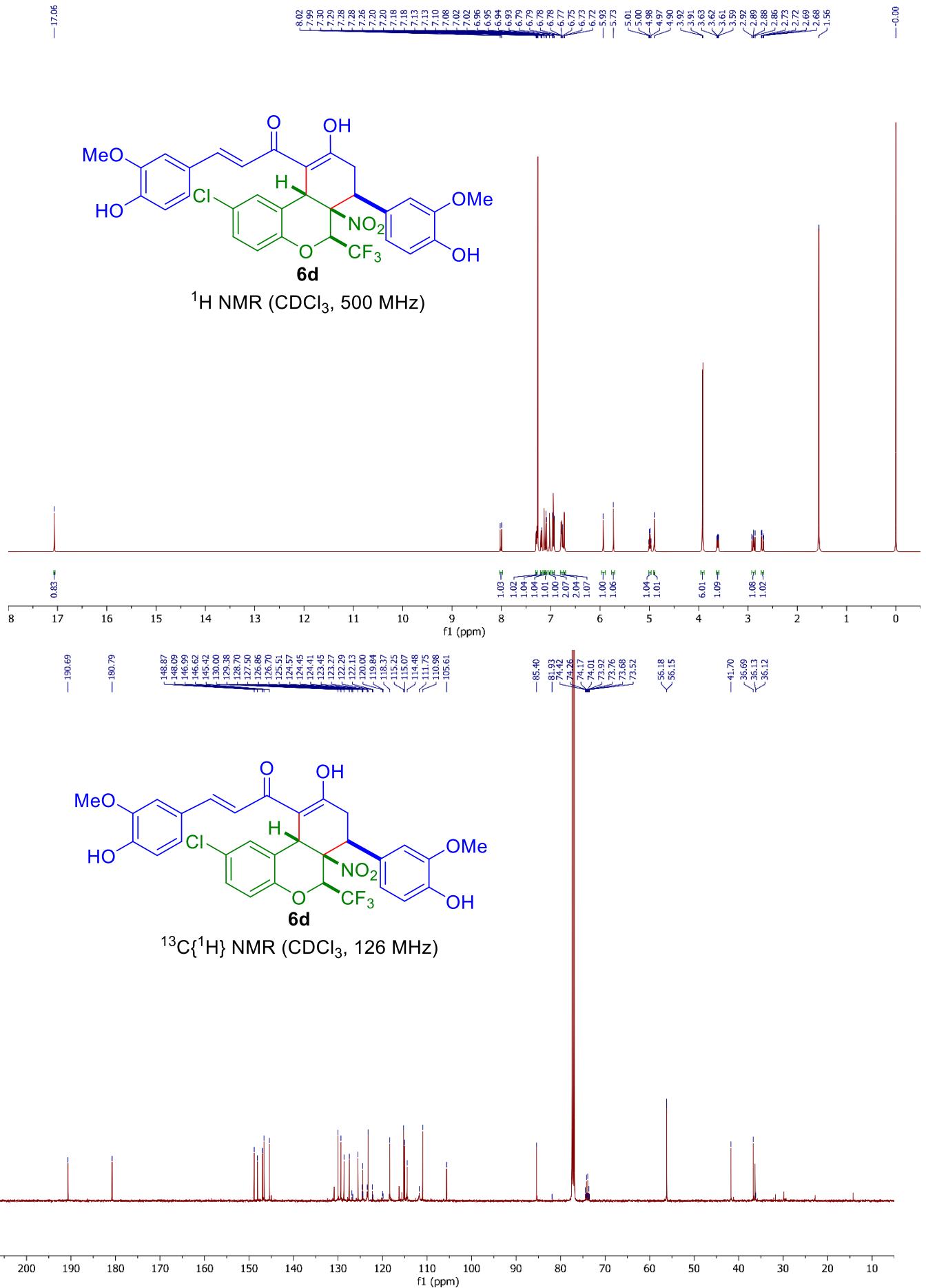


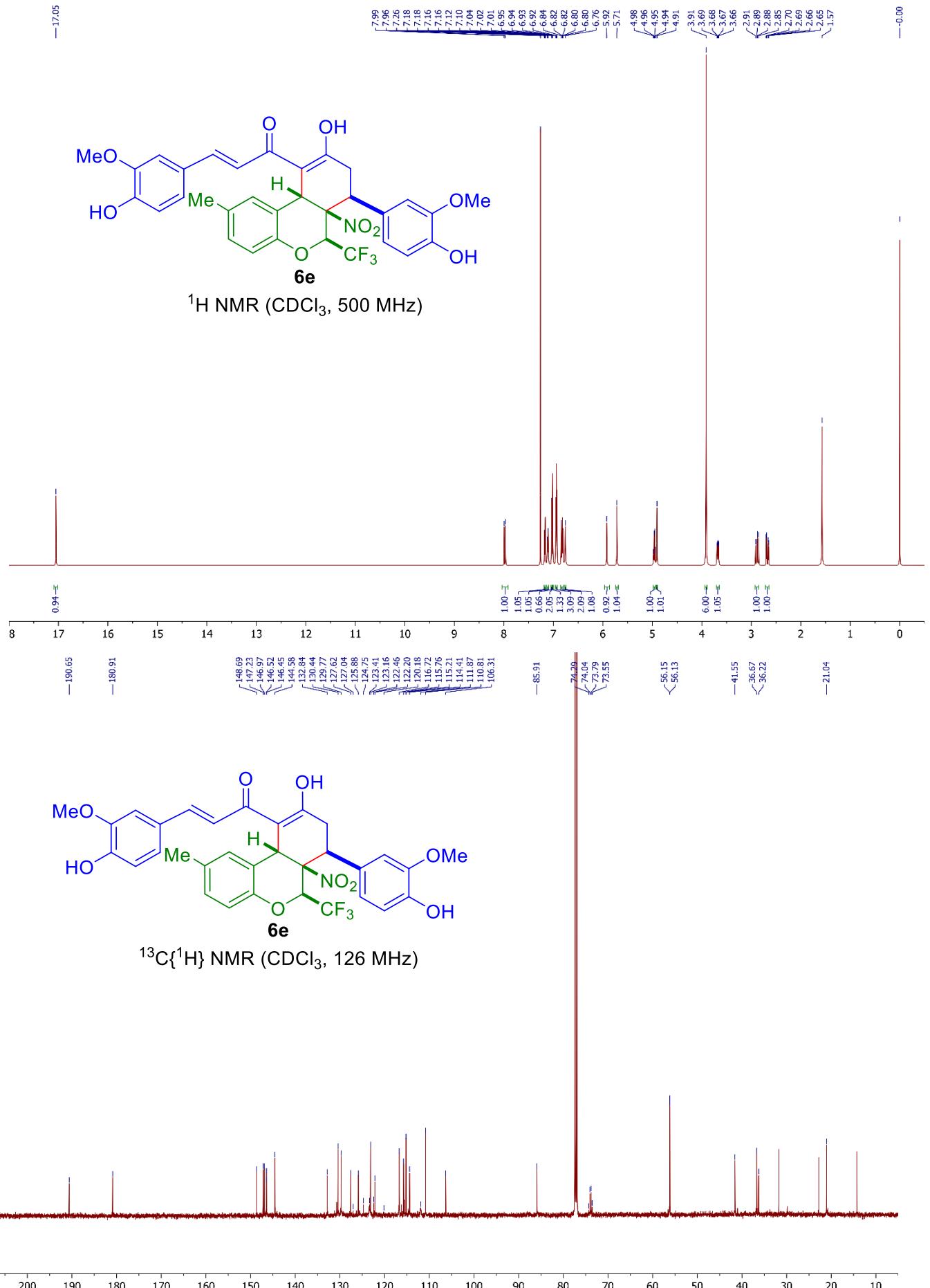


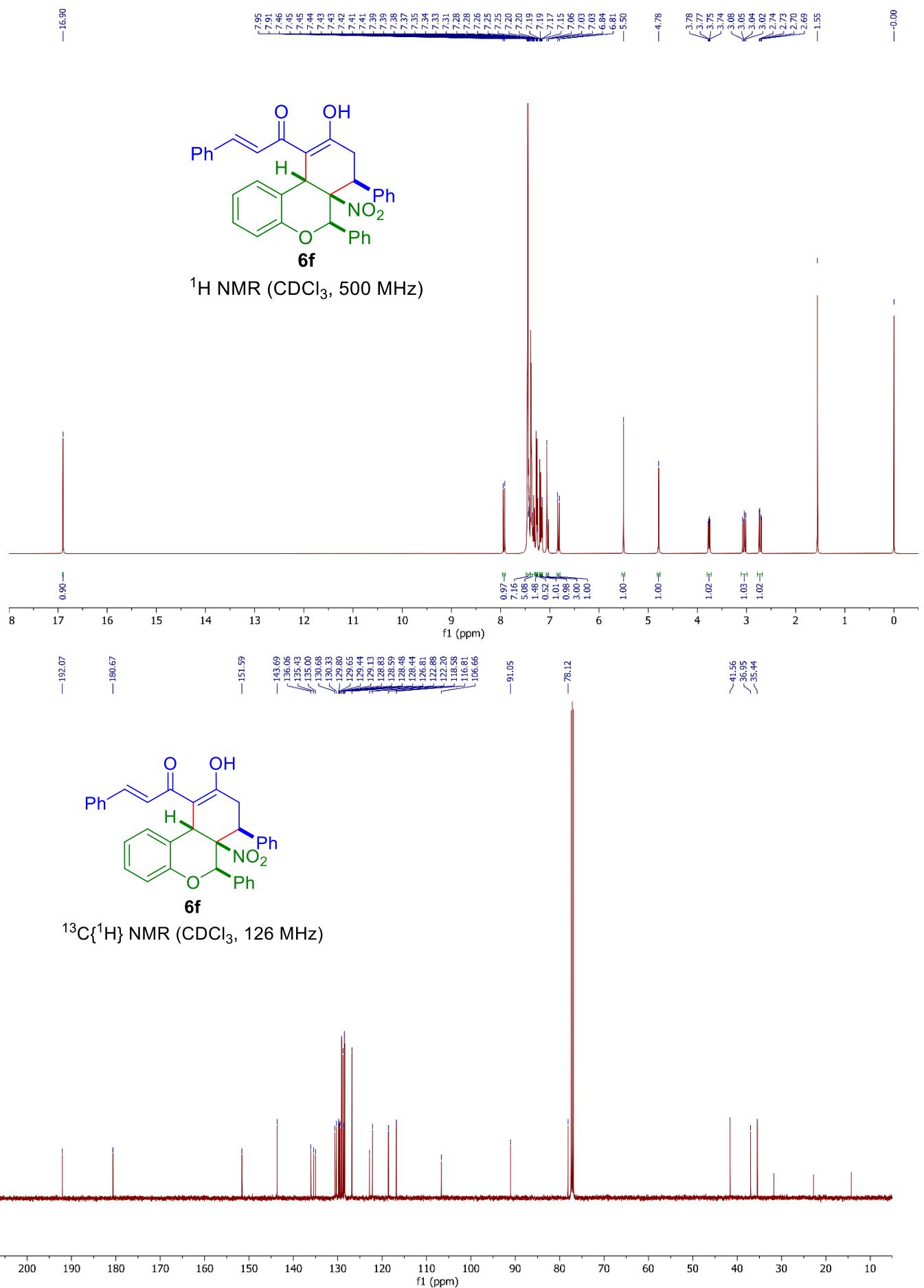


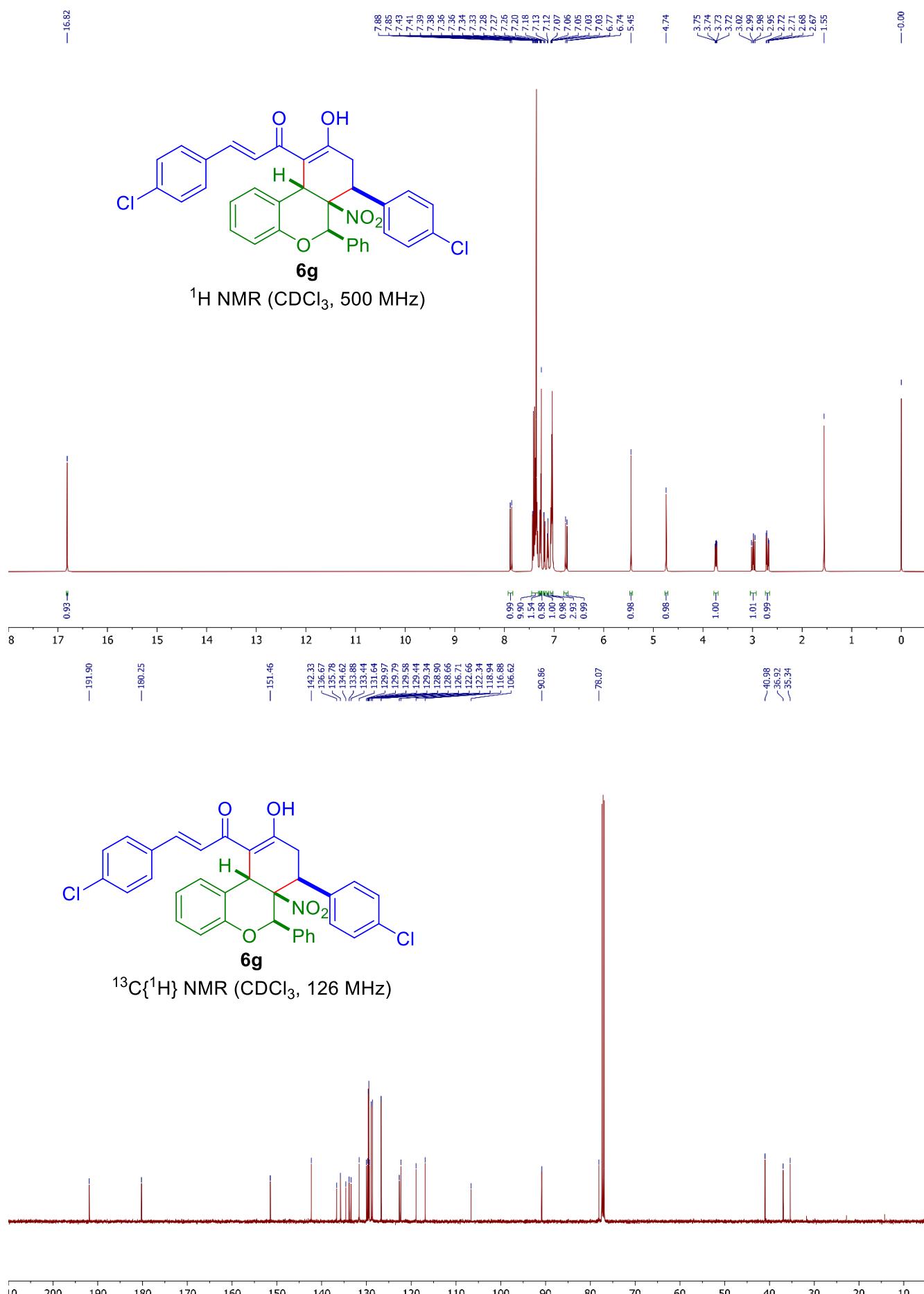


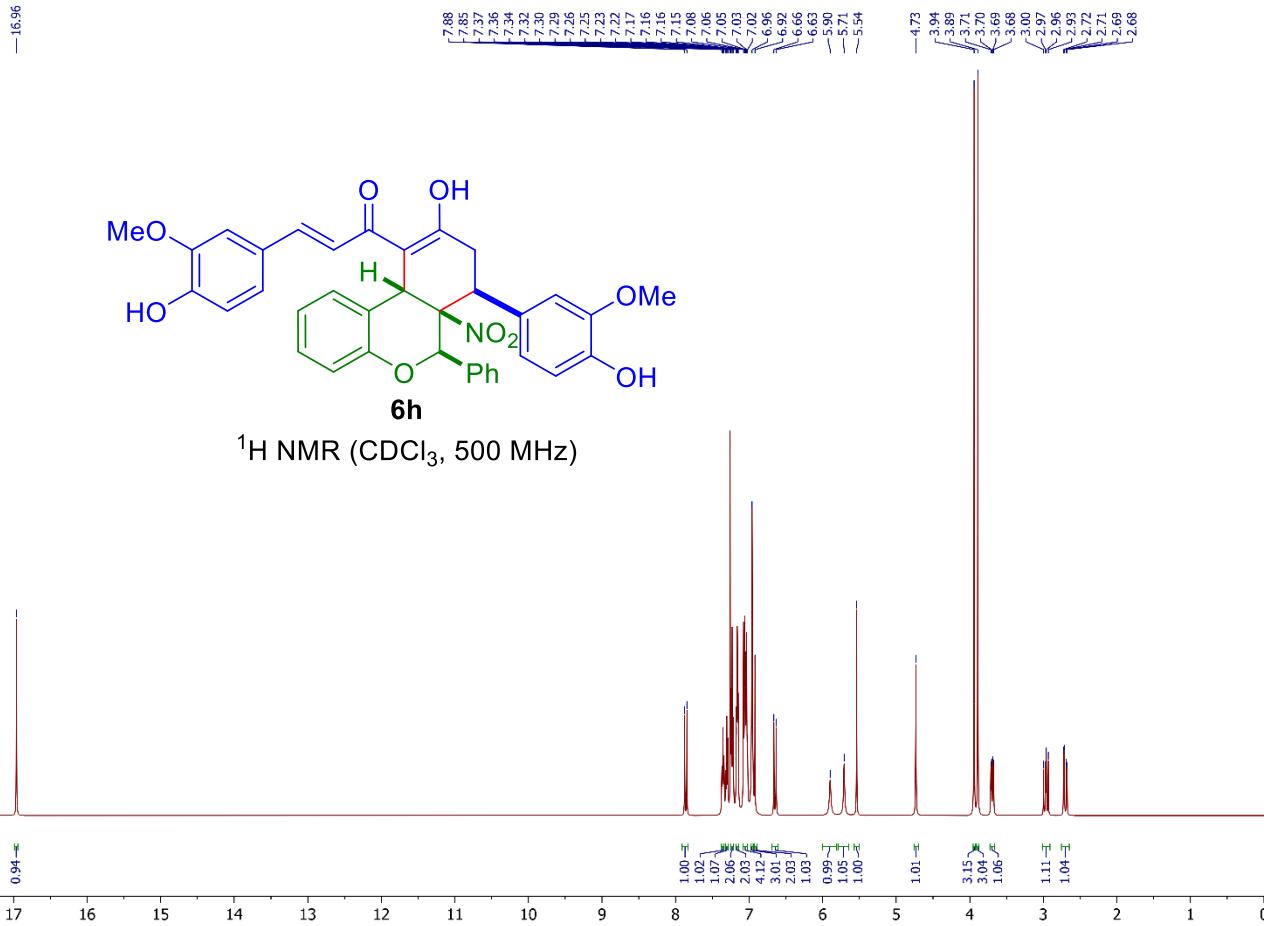


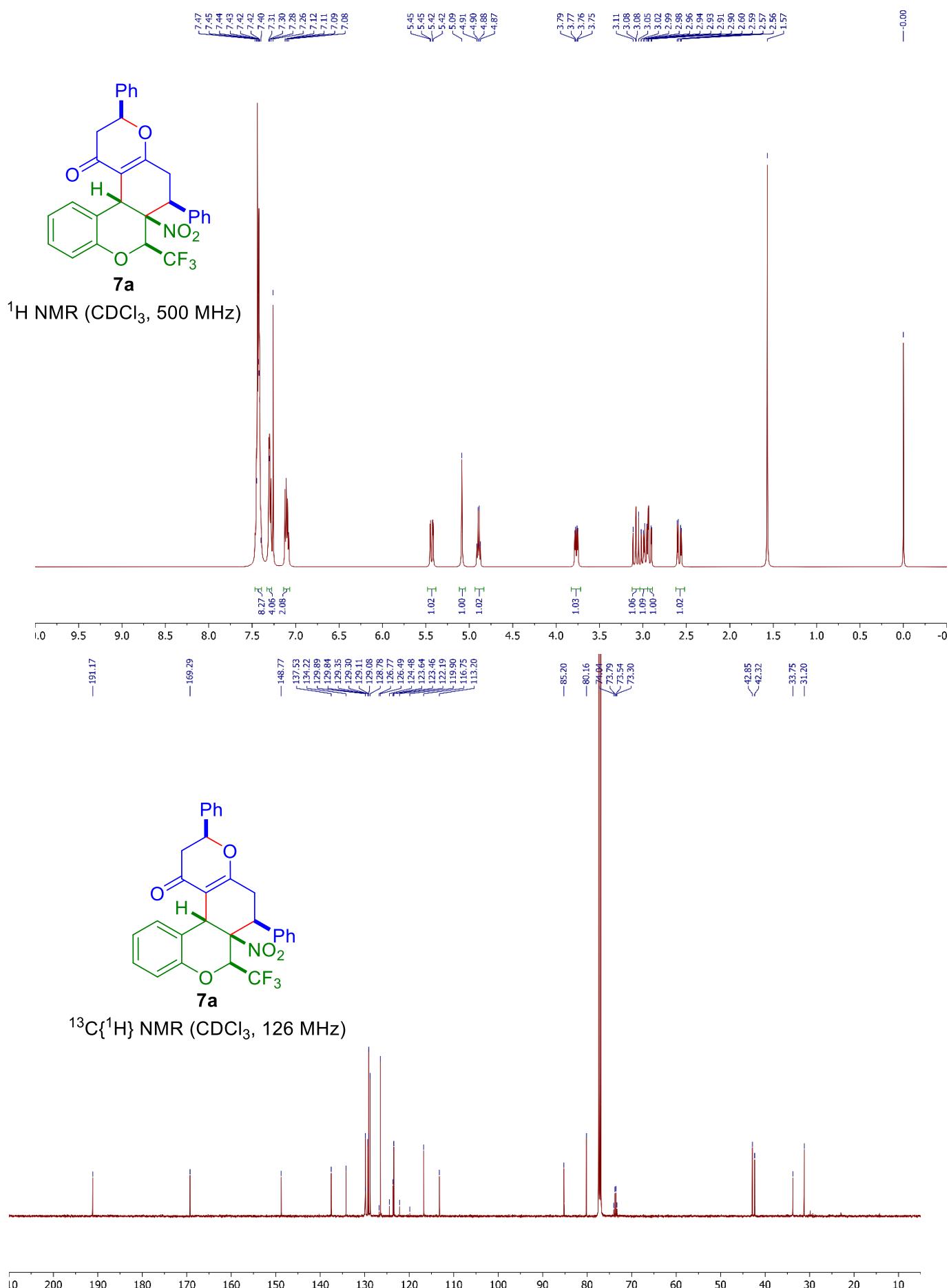


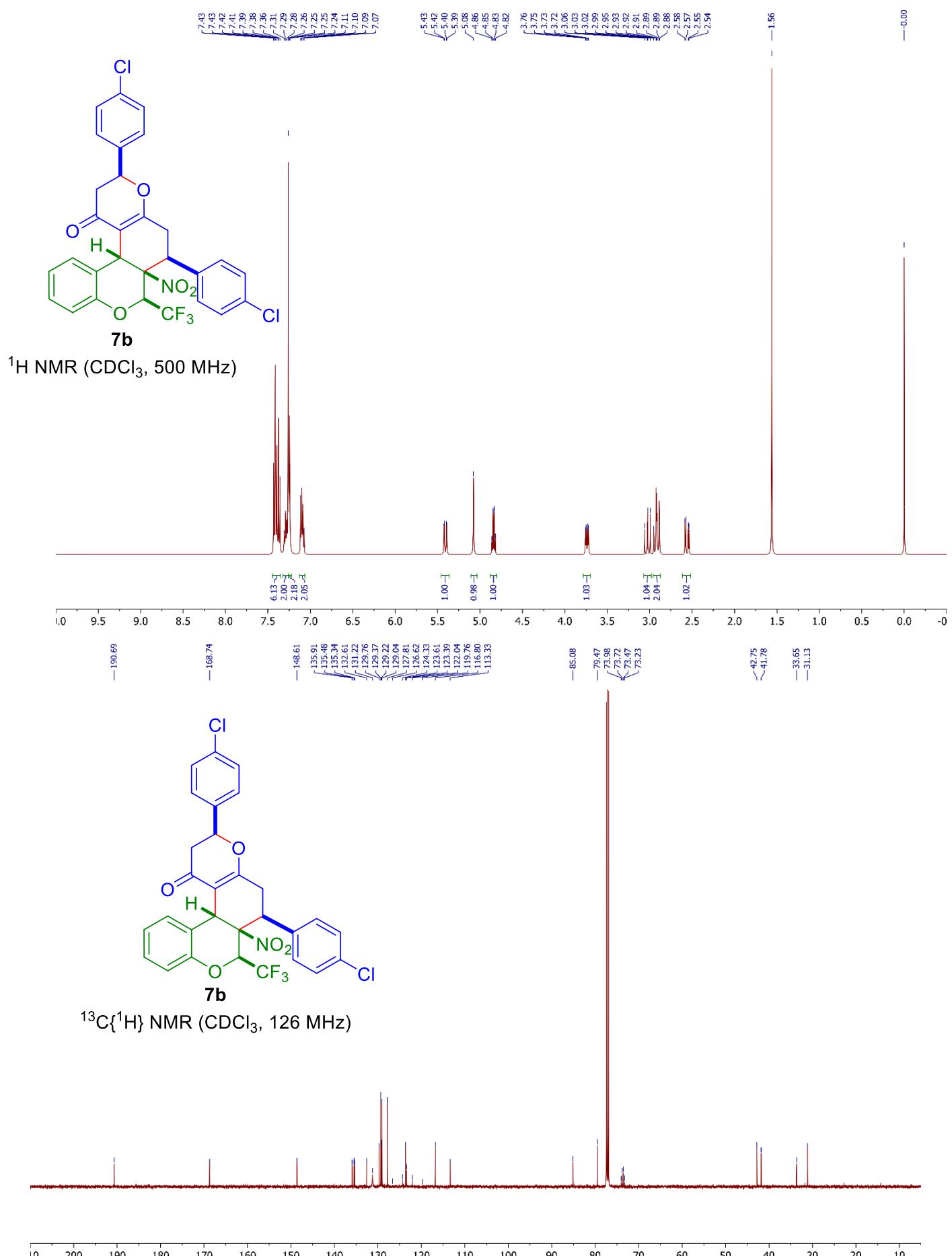


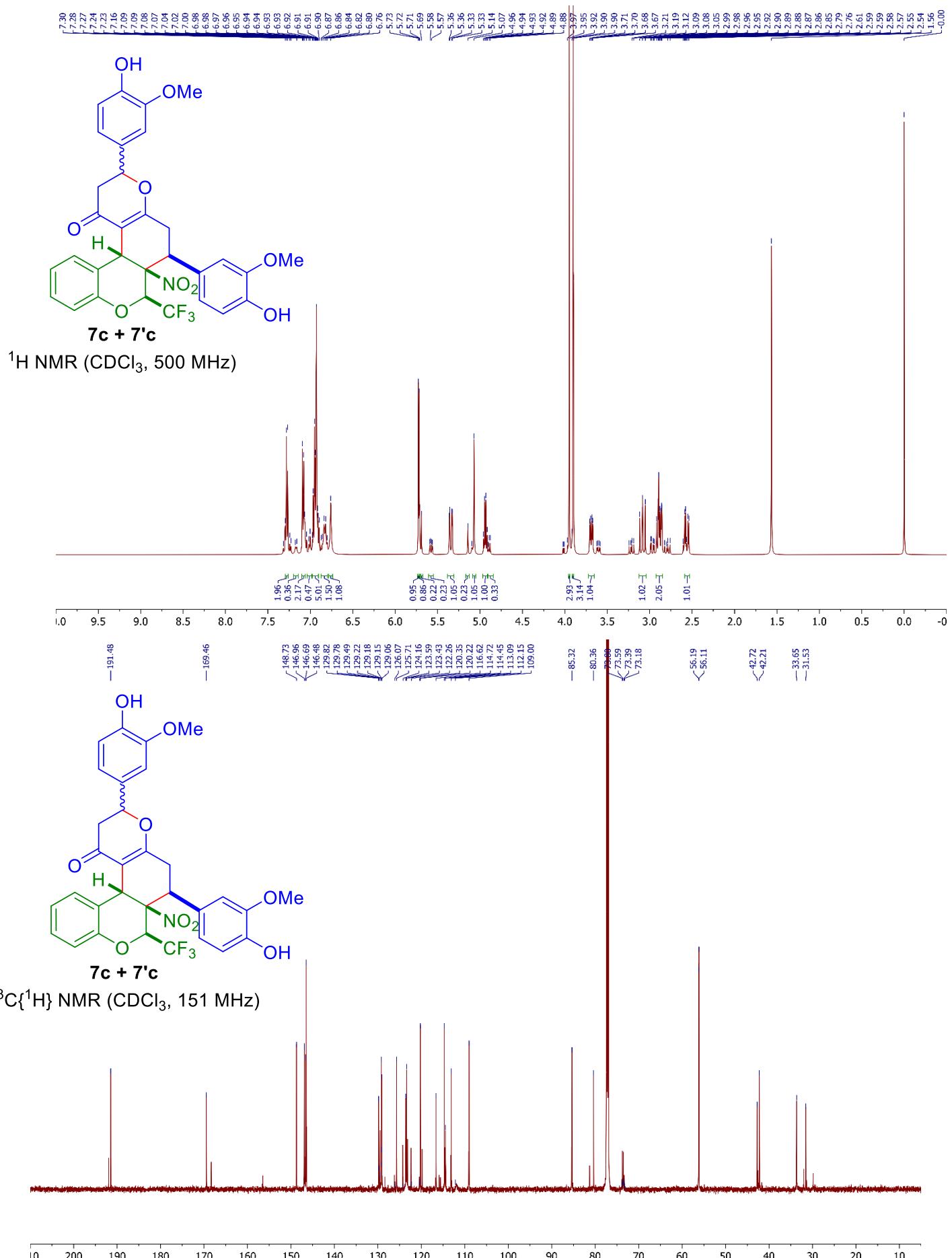


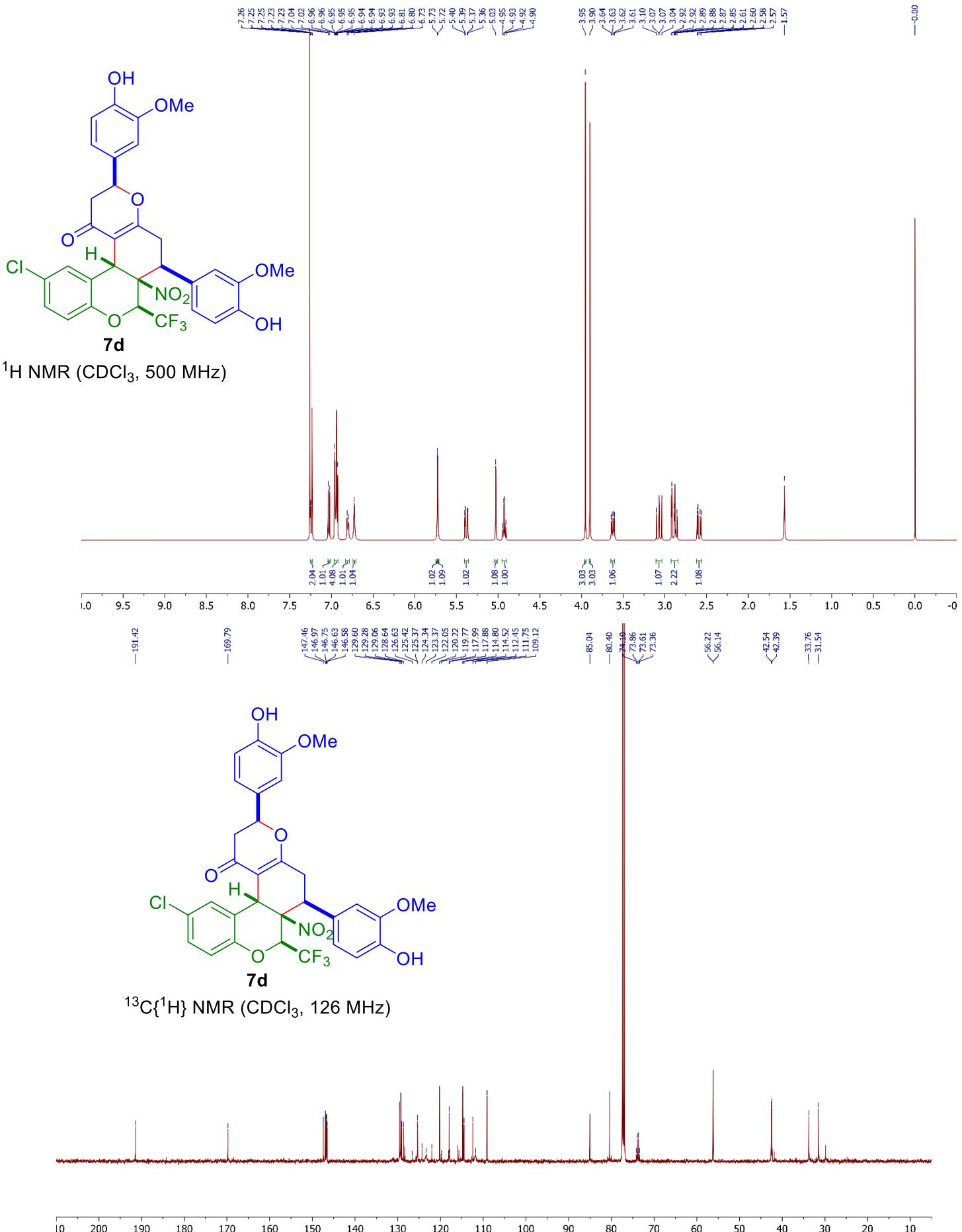


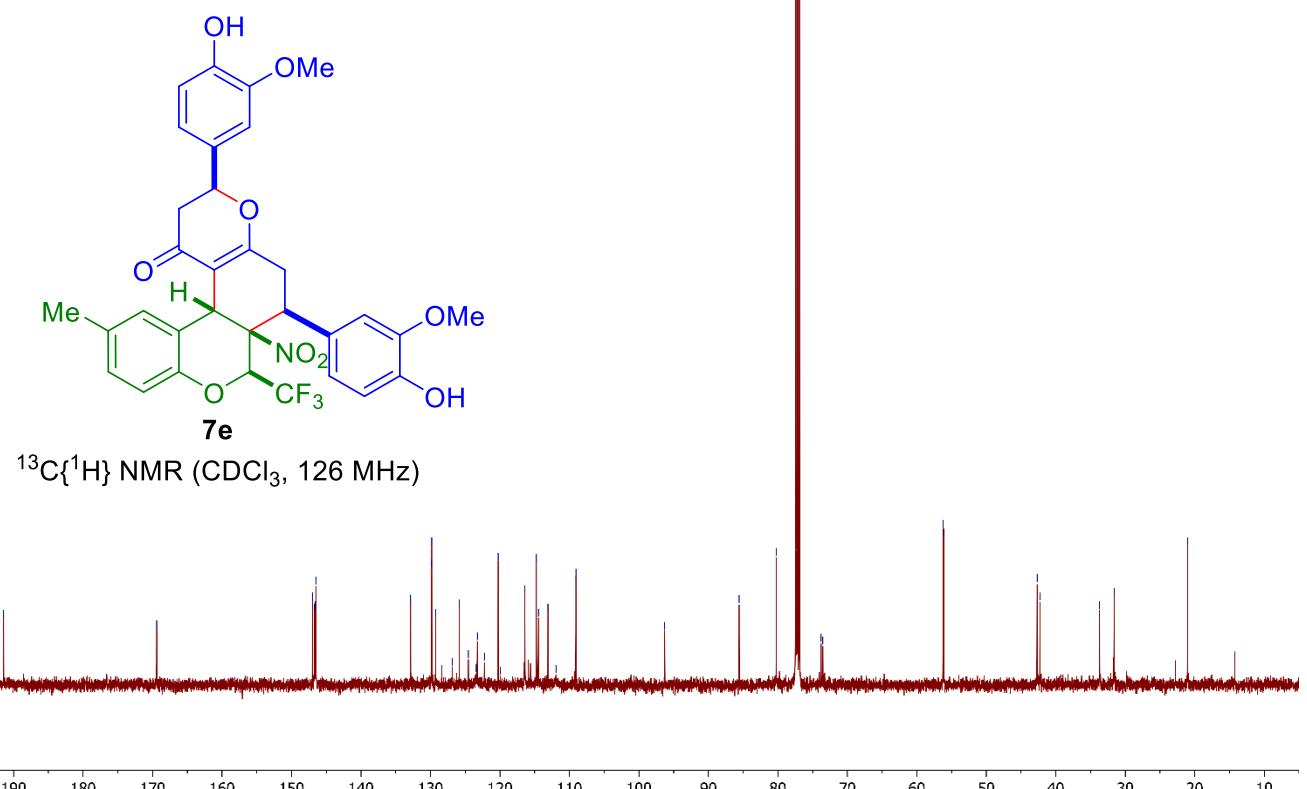
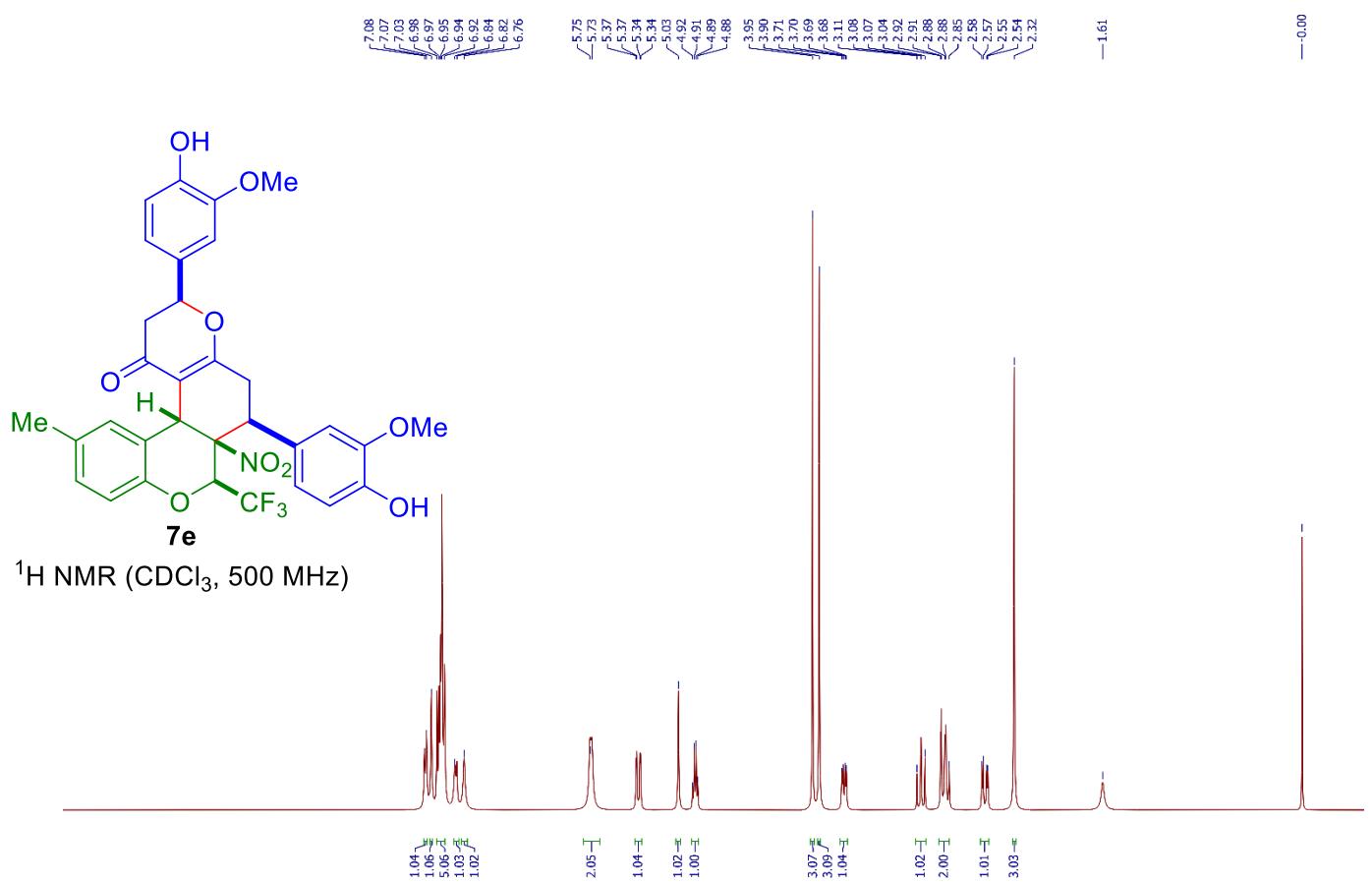


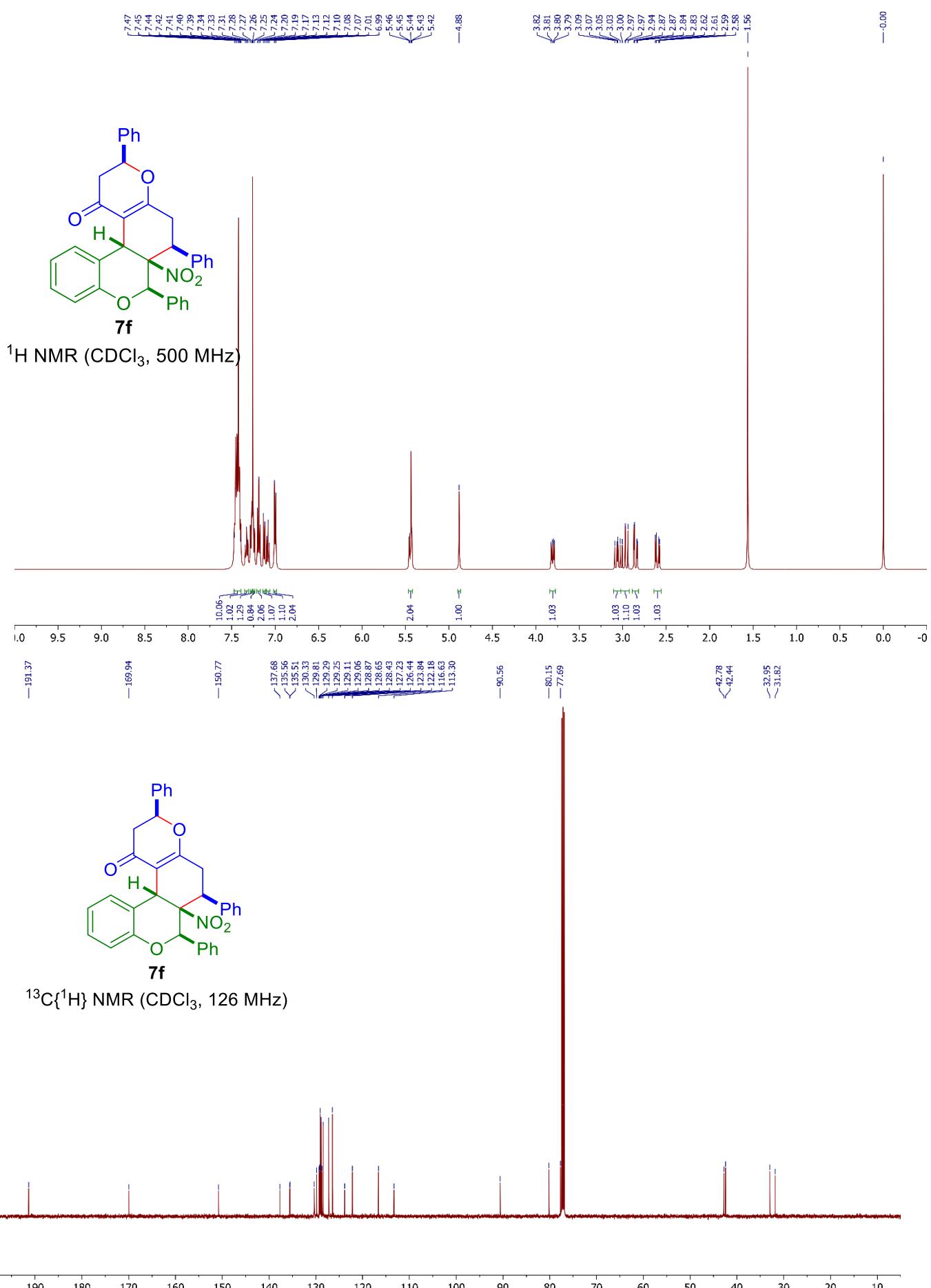


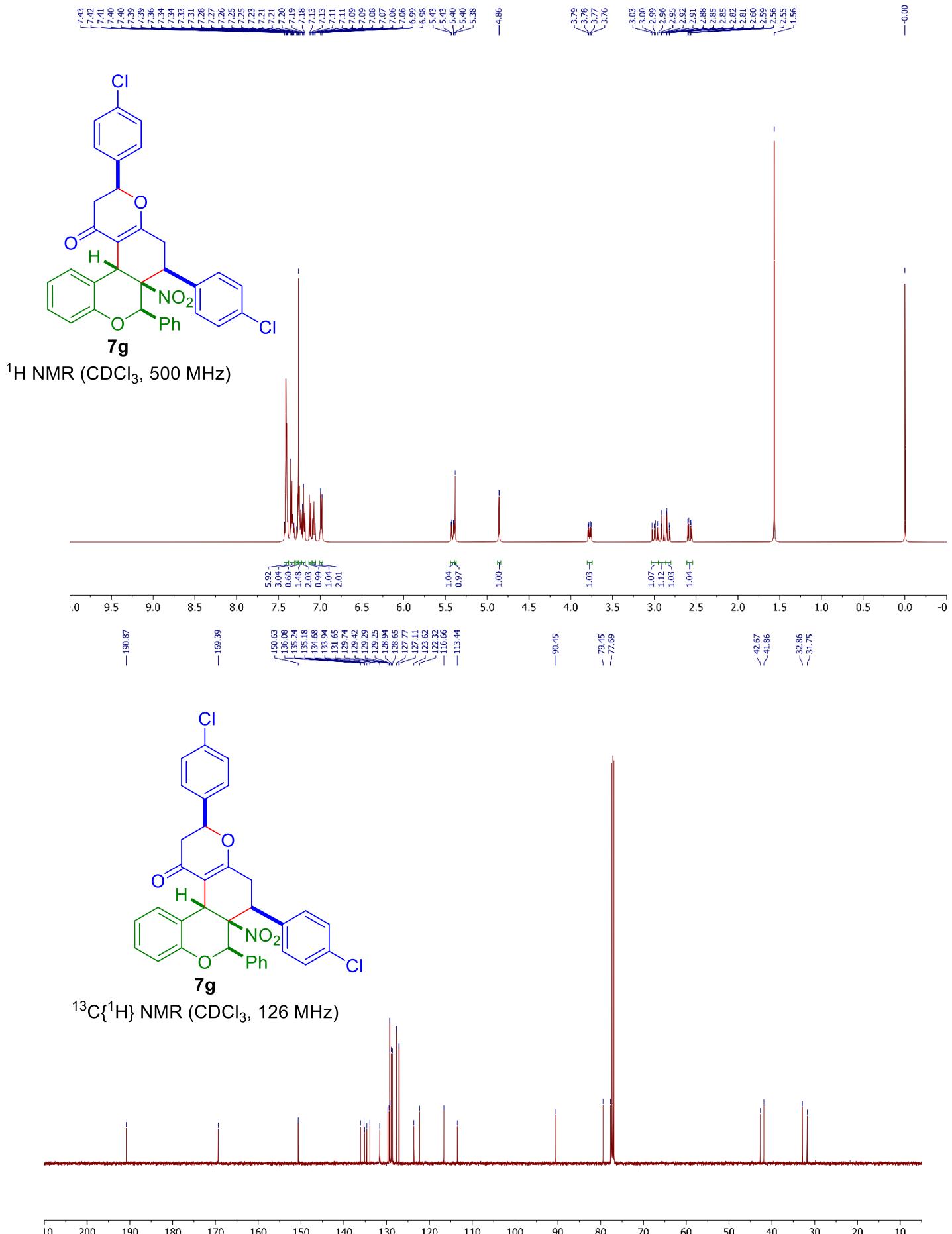


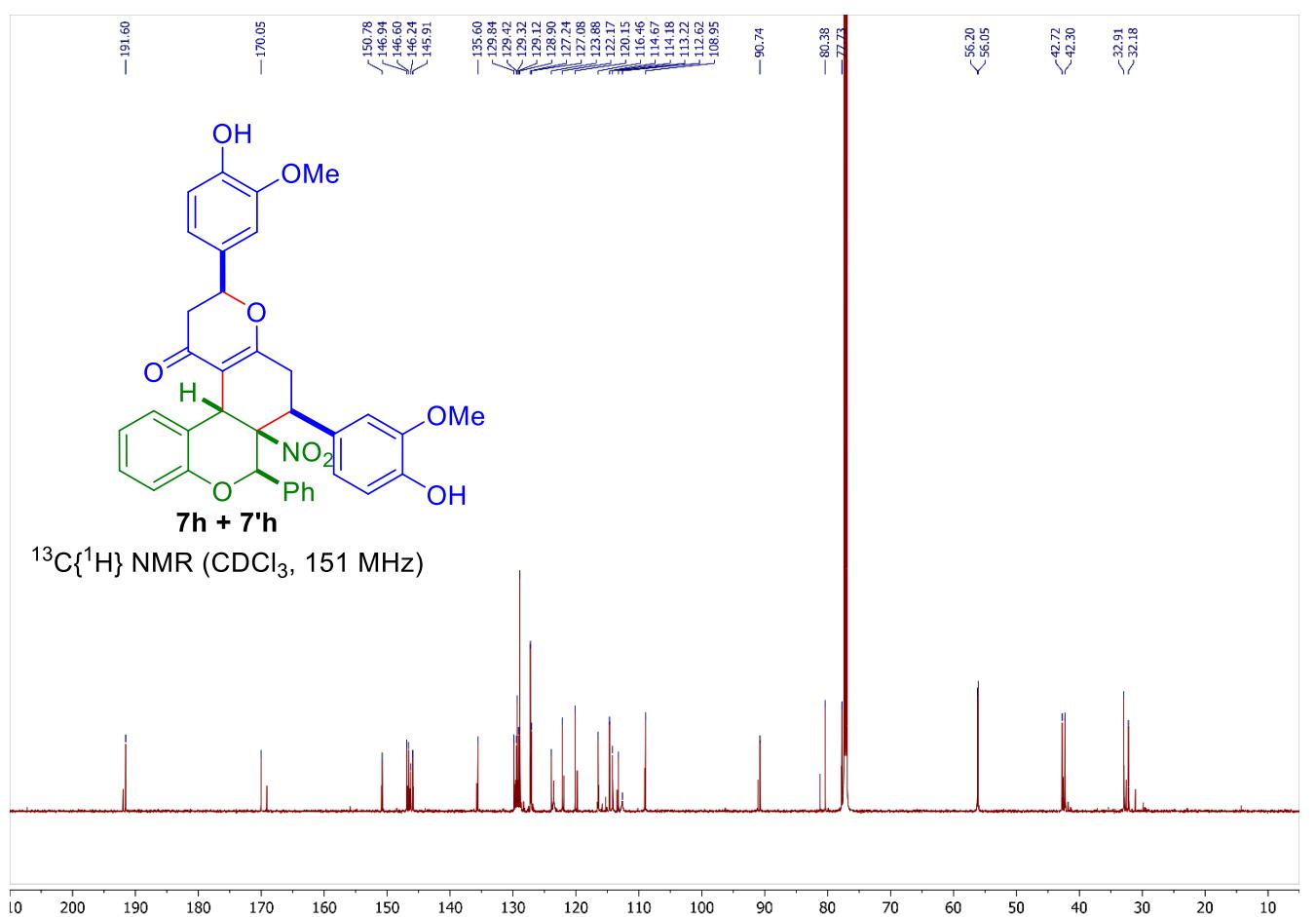
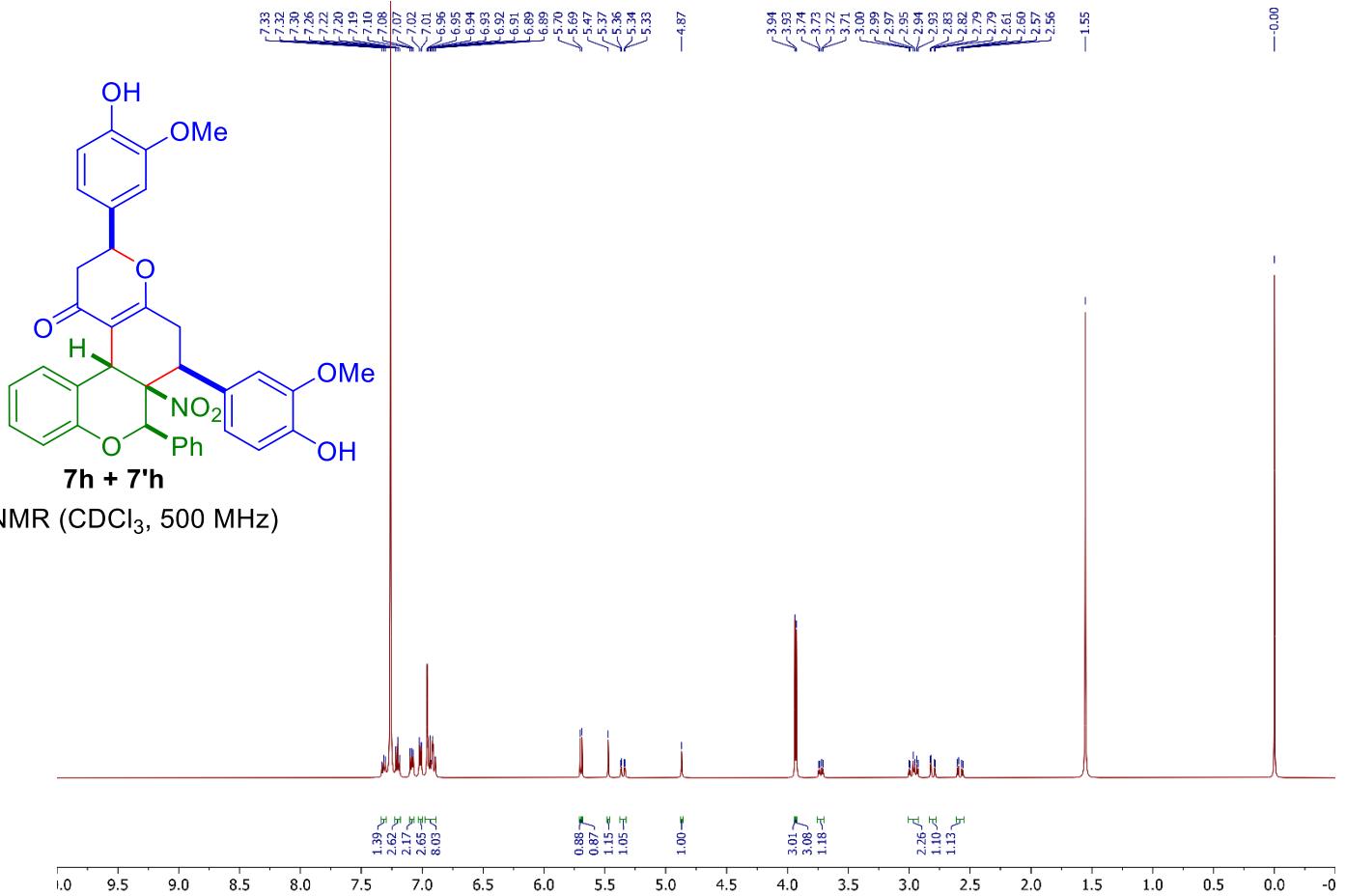


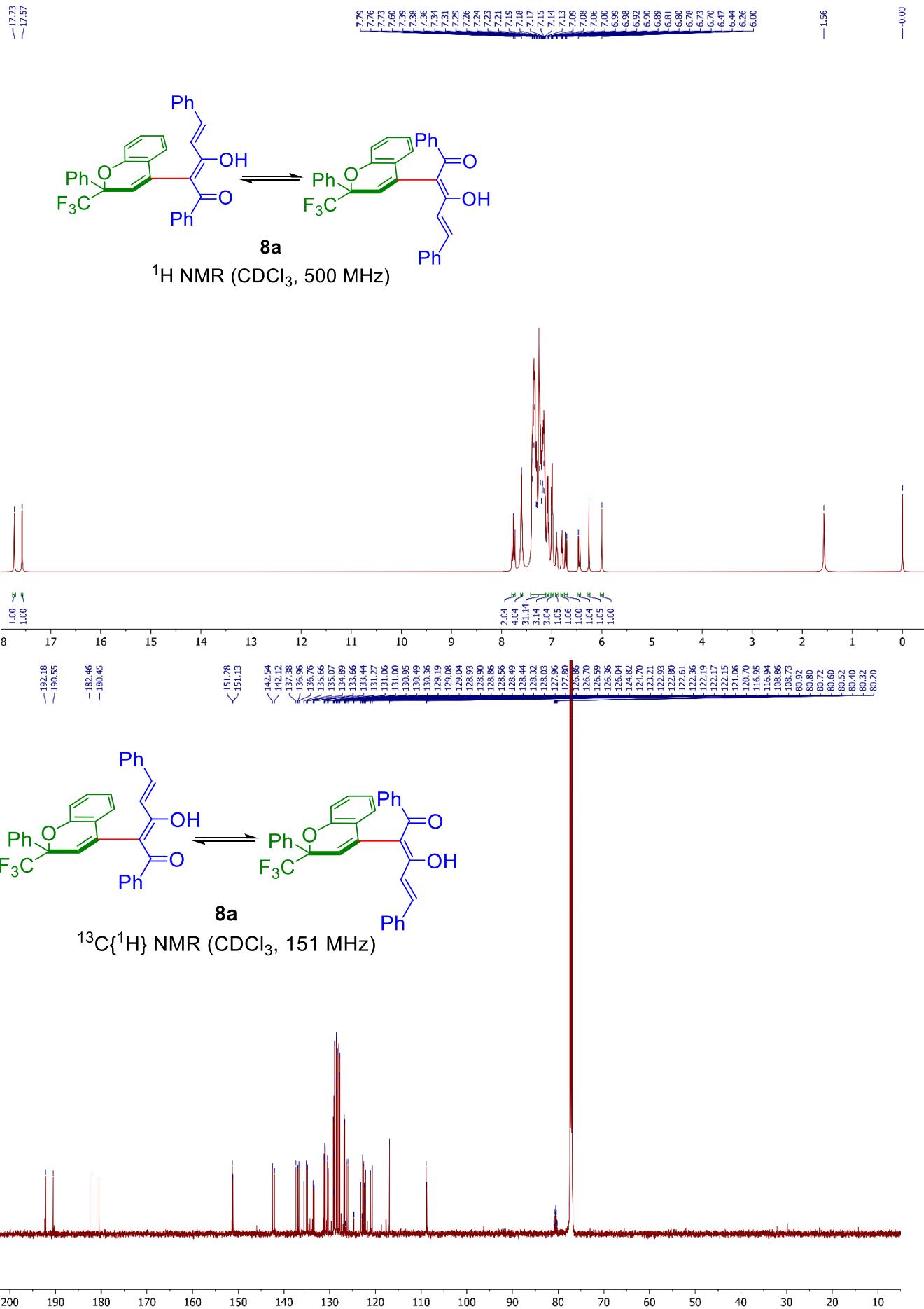


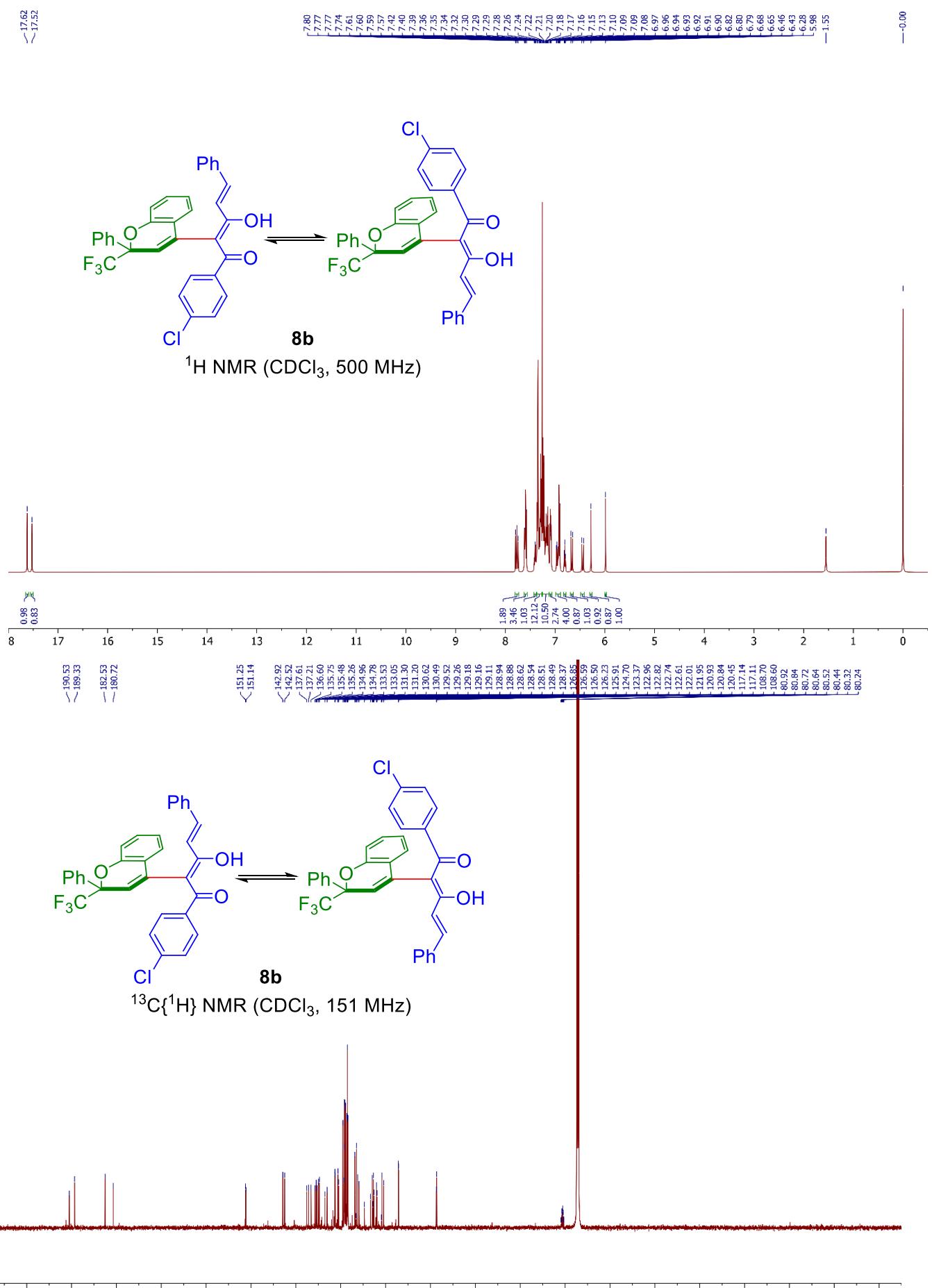


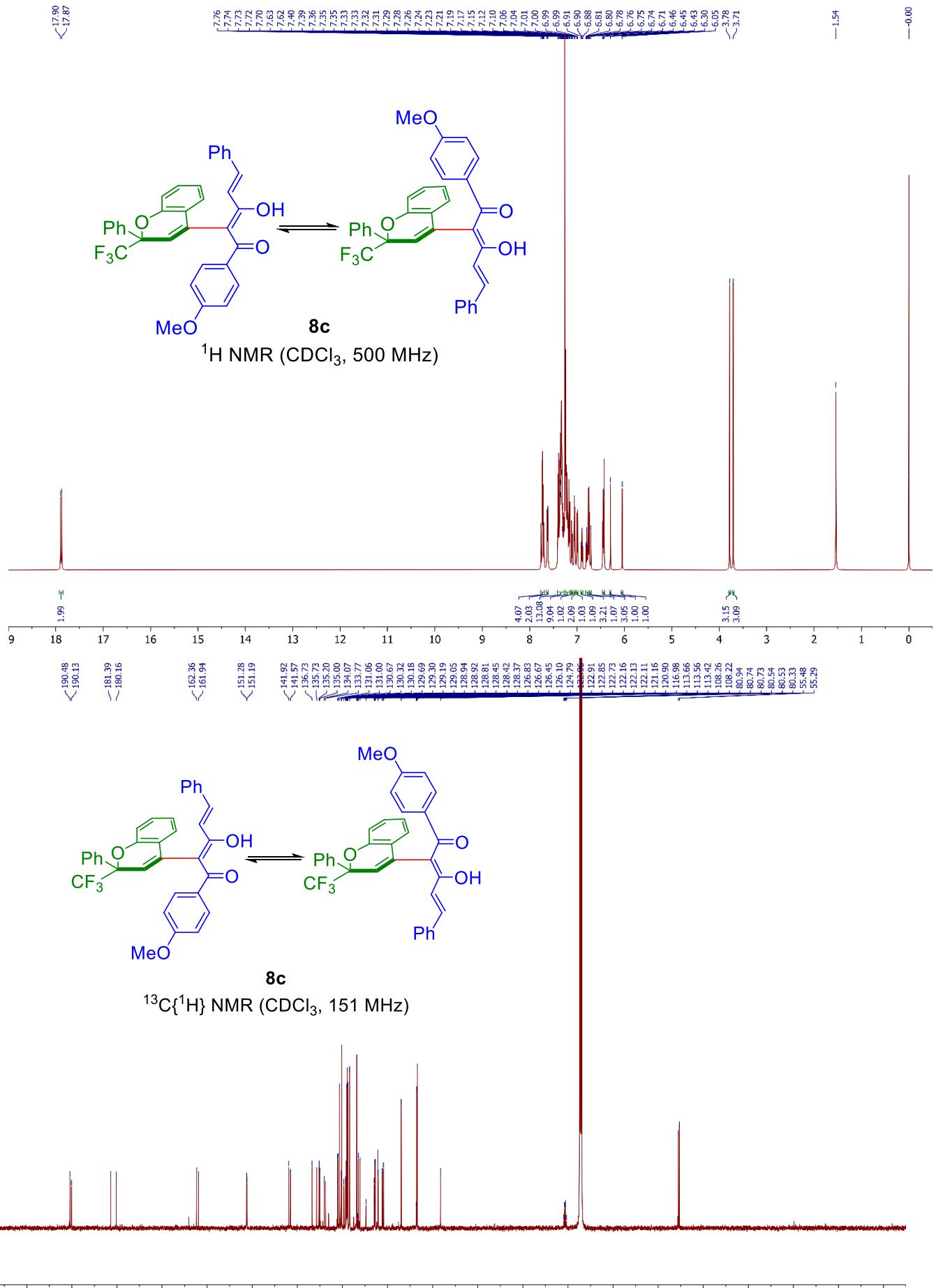


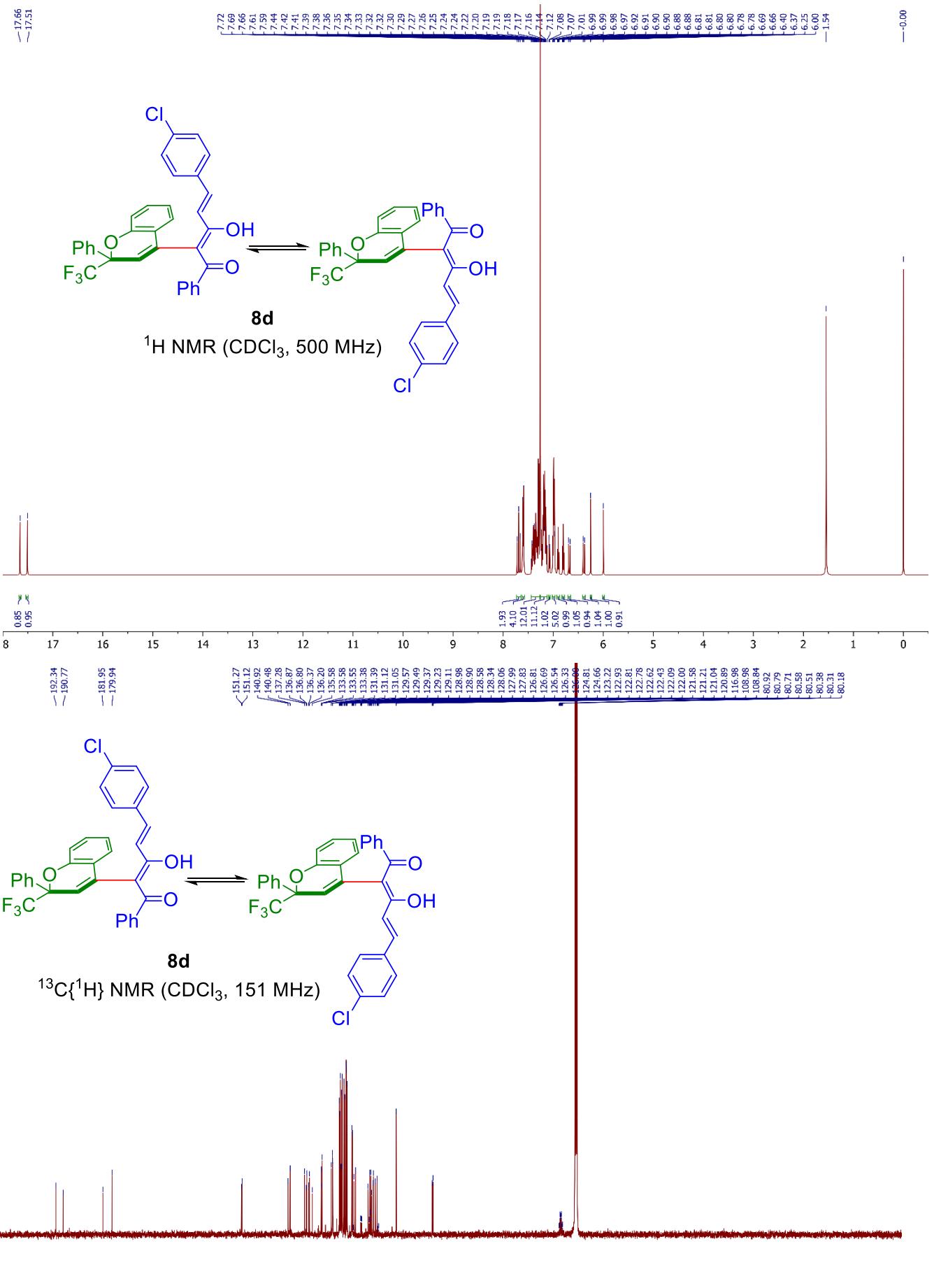


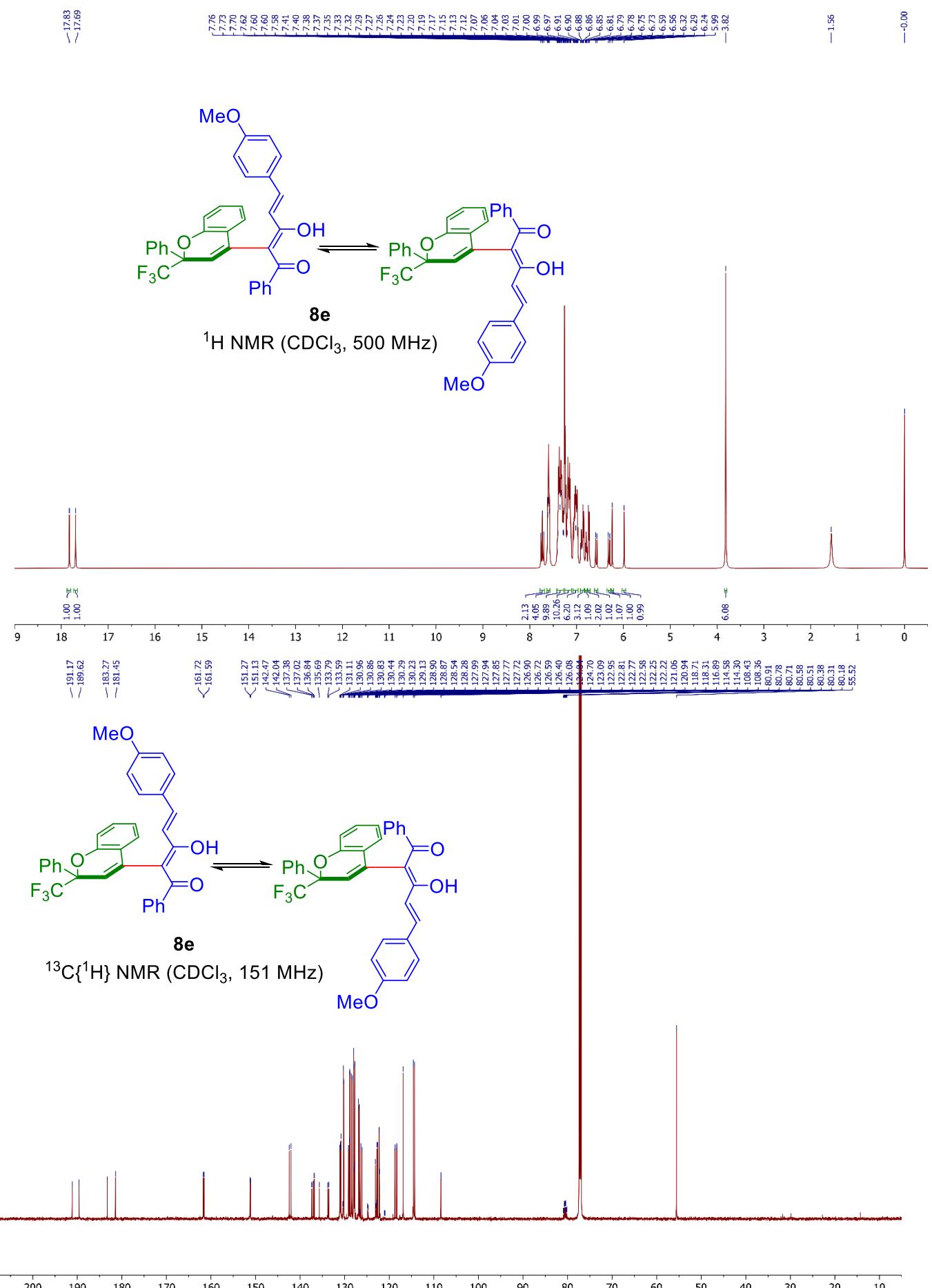


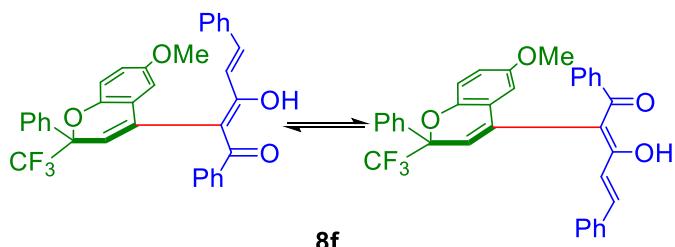
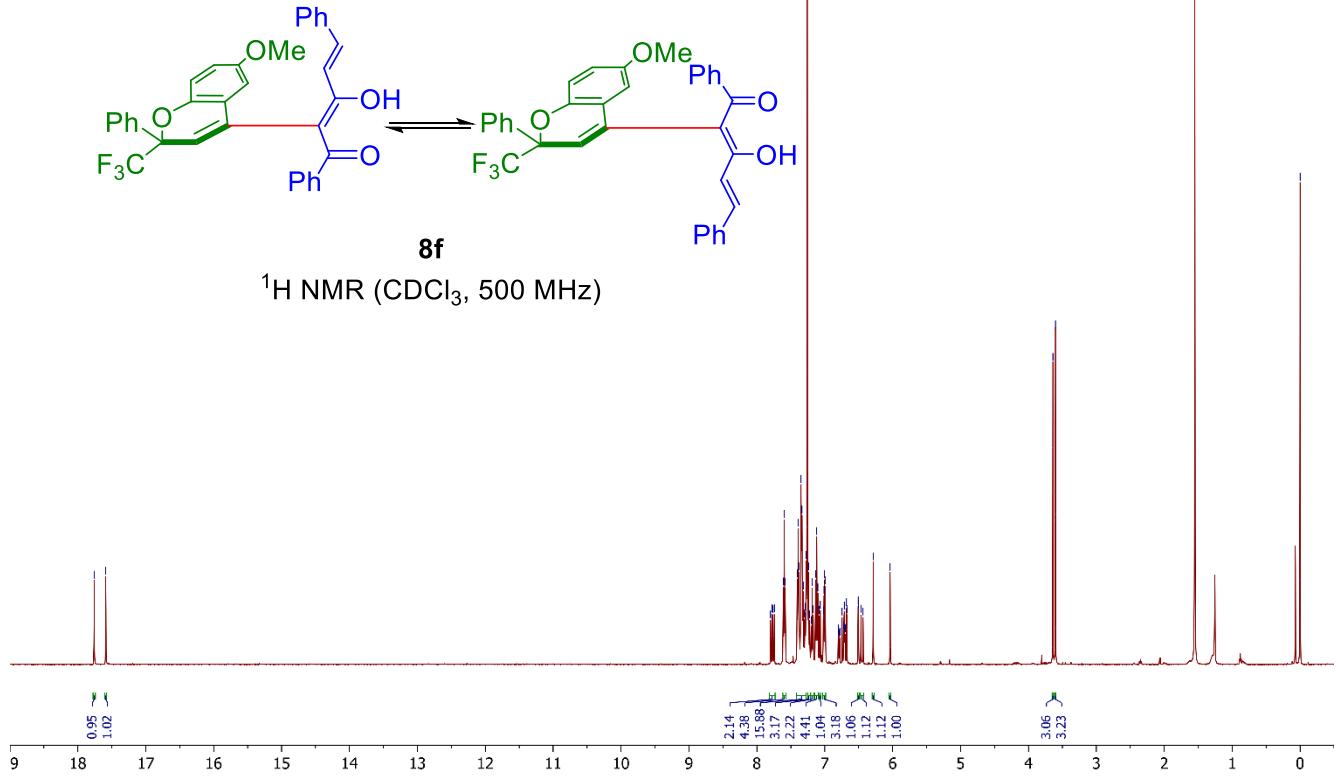
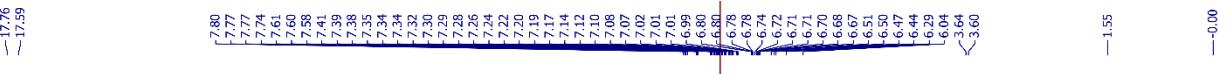




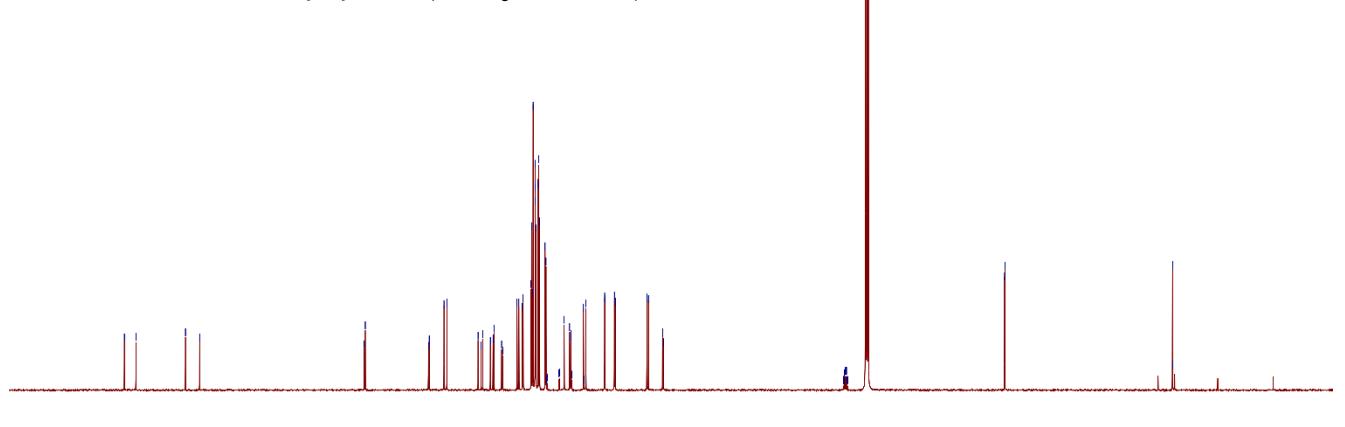


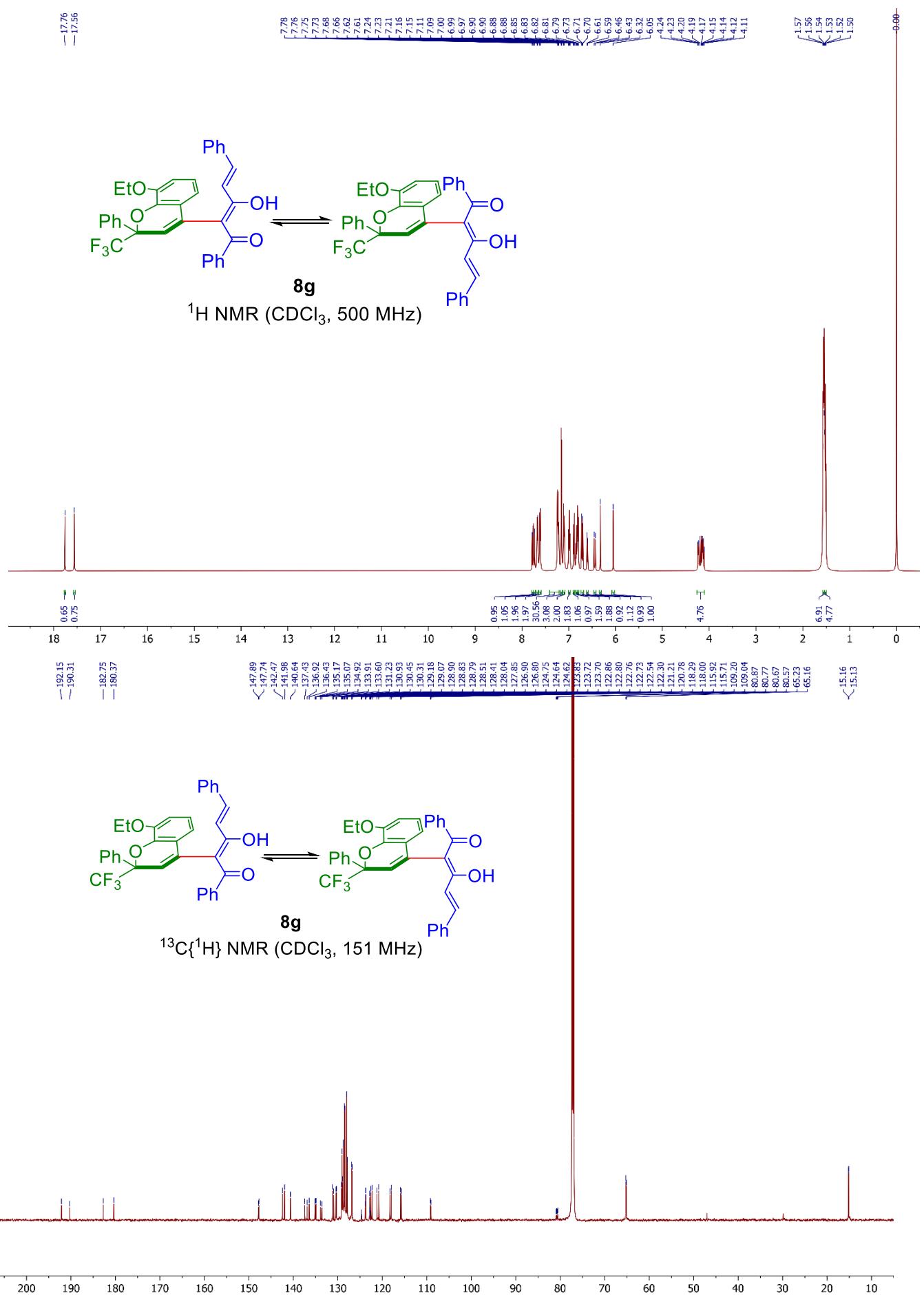


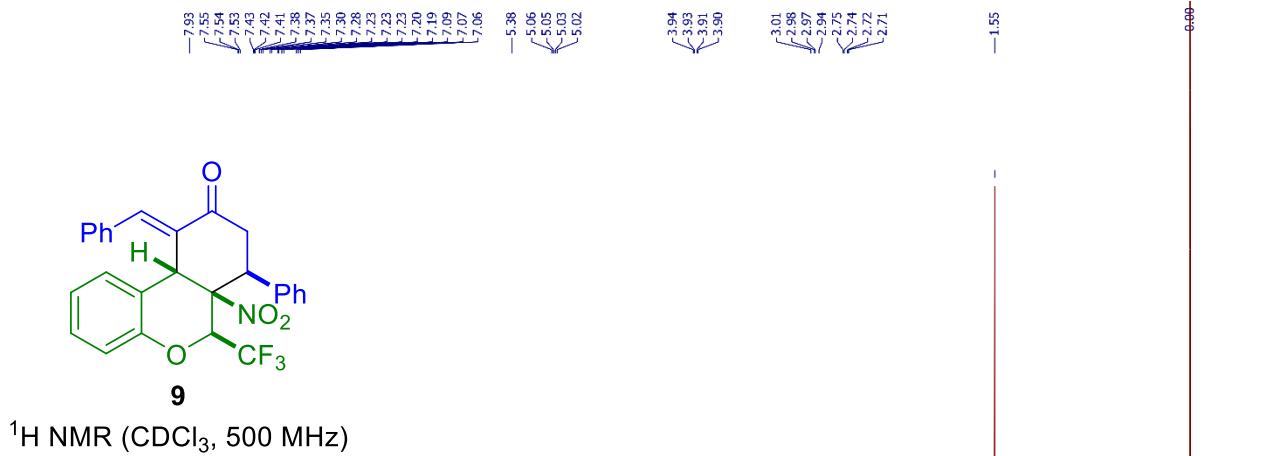




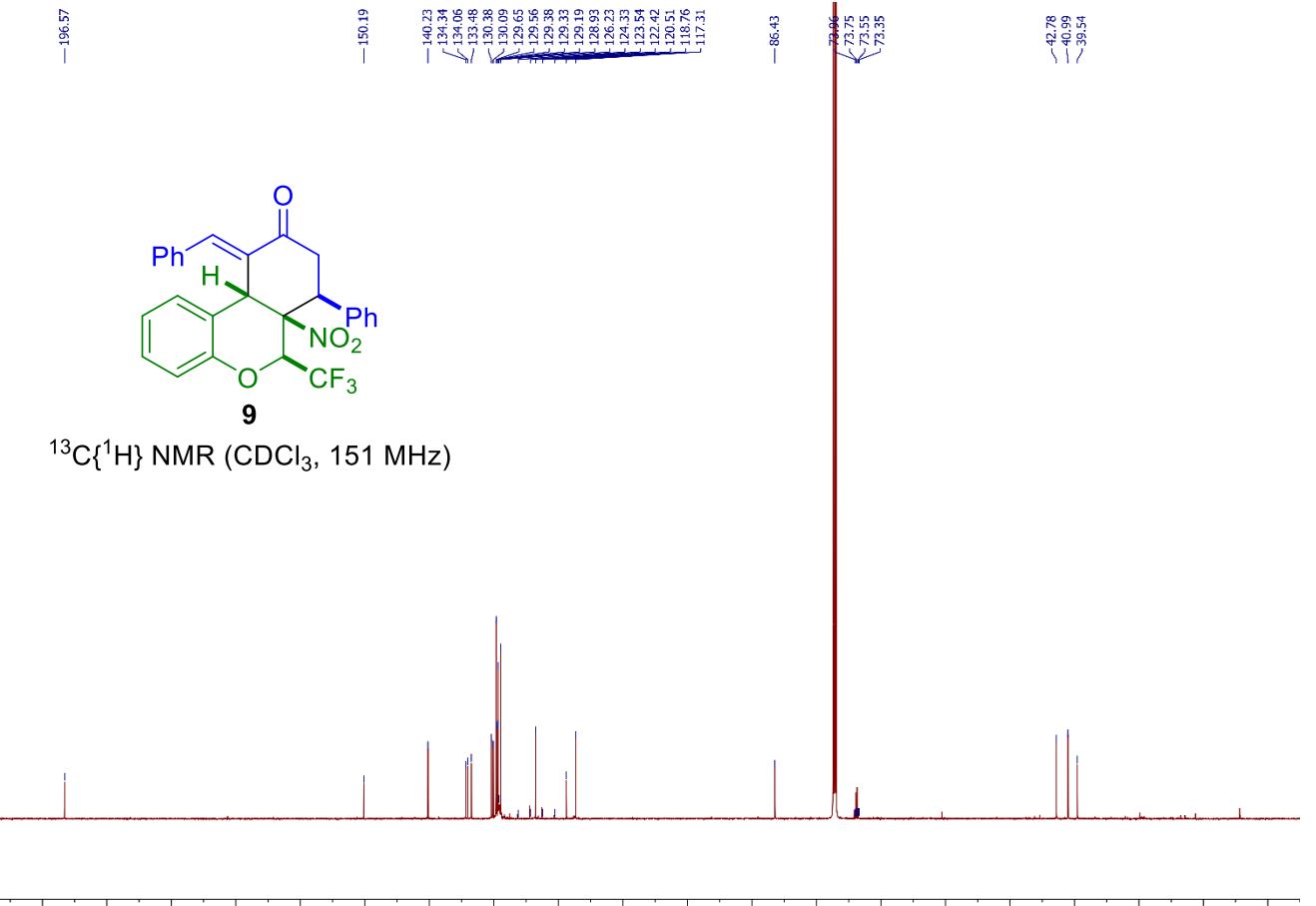
¹³C{¹H} NMR (CDCl_3 , 151 MHz)

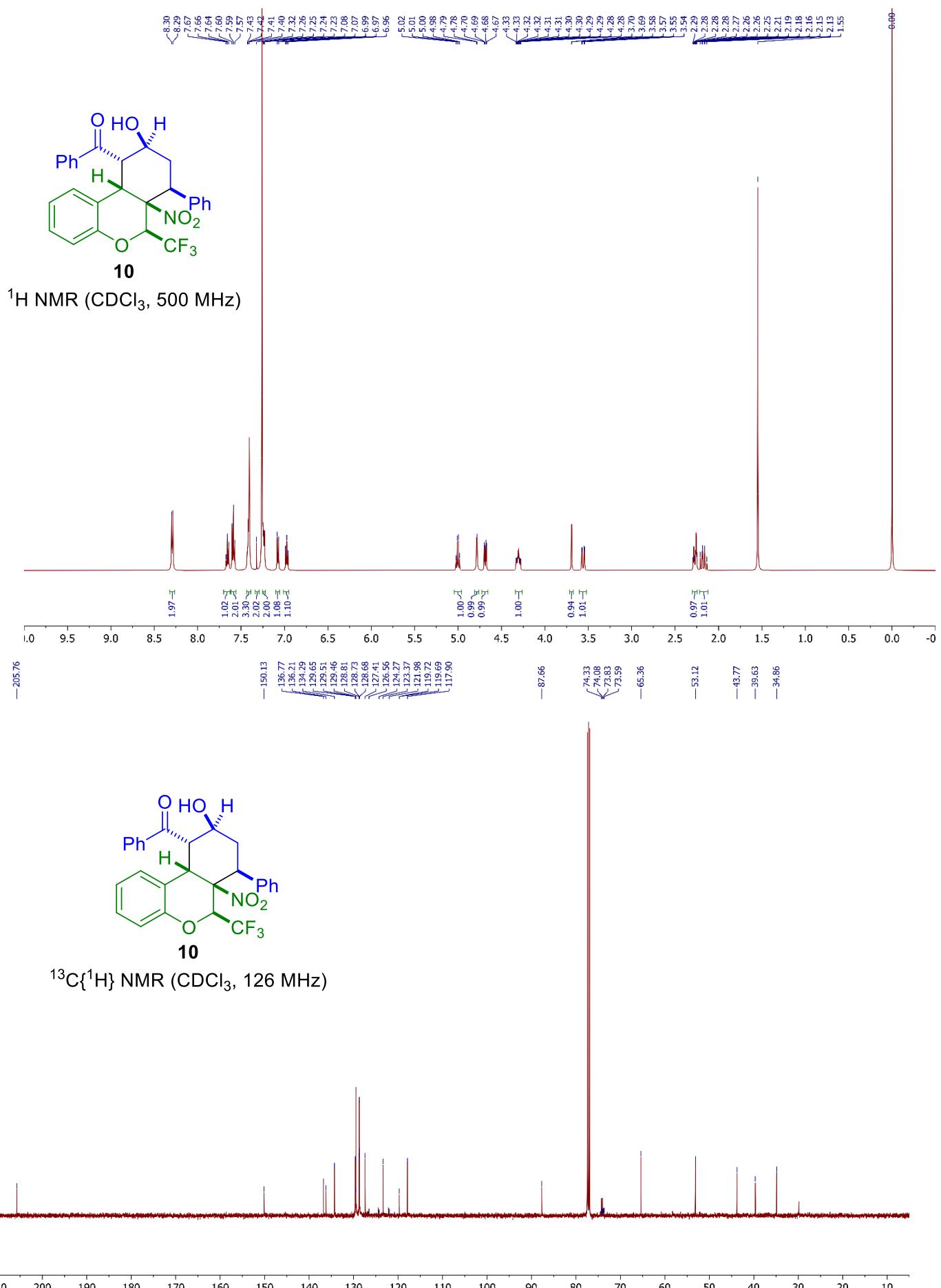


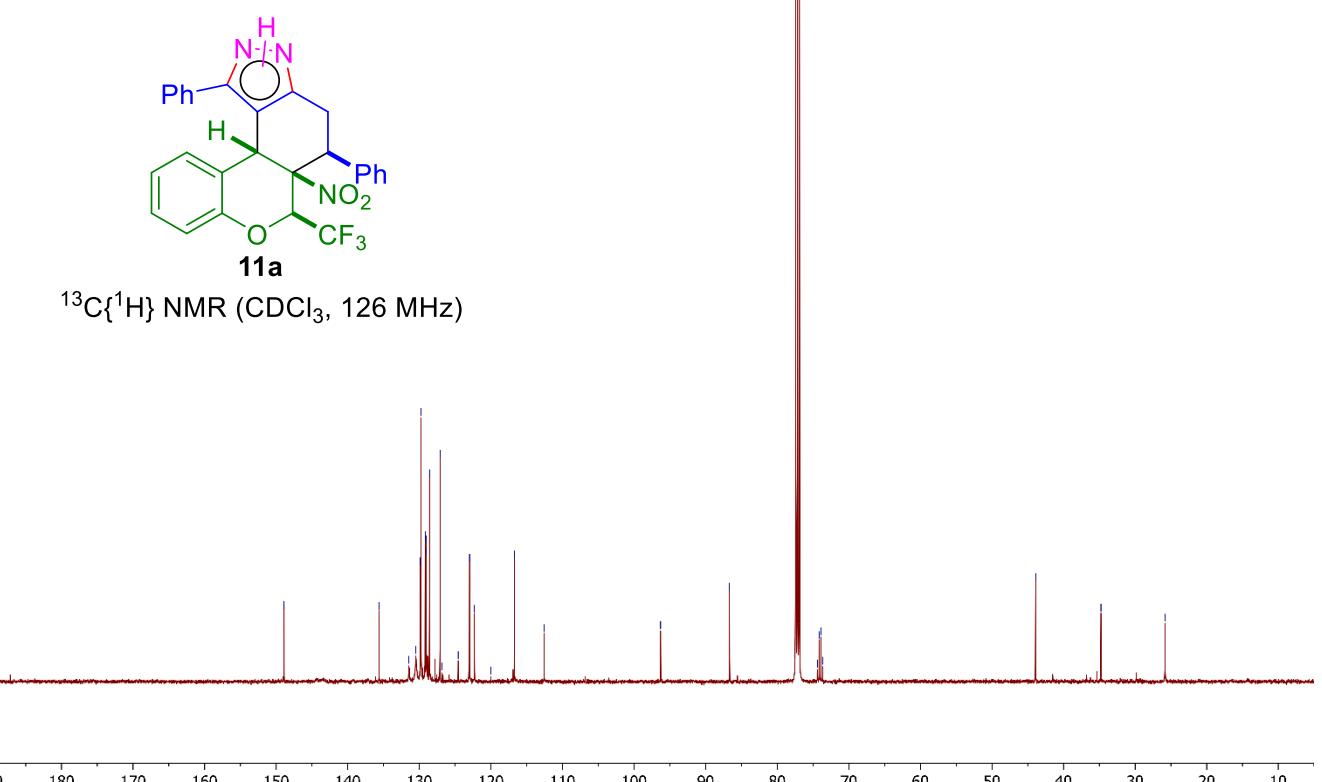
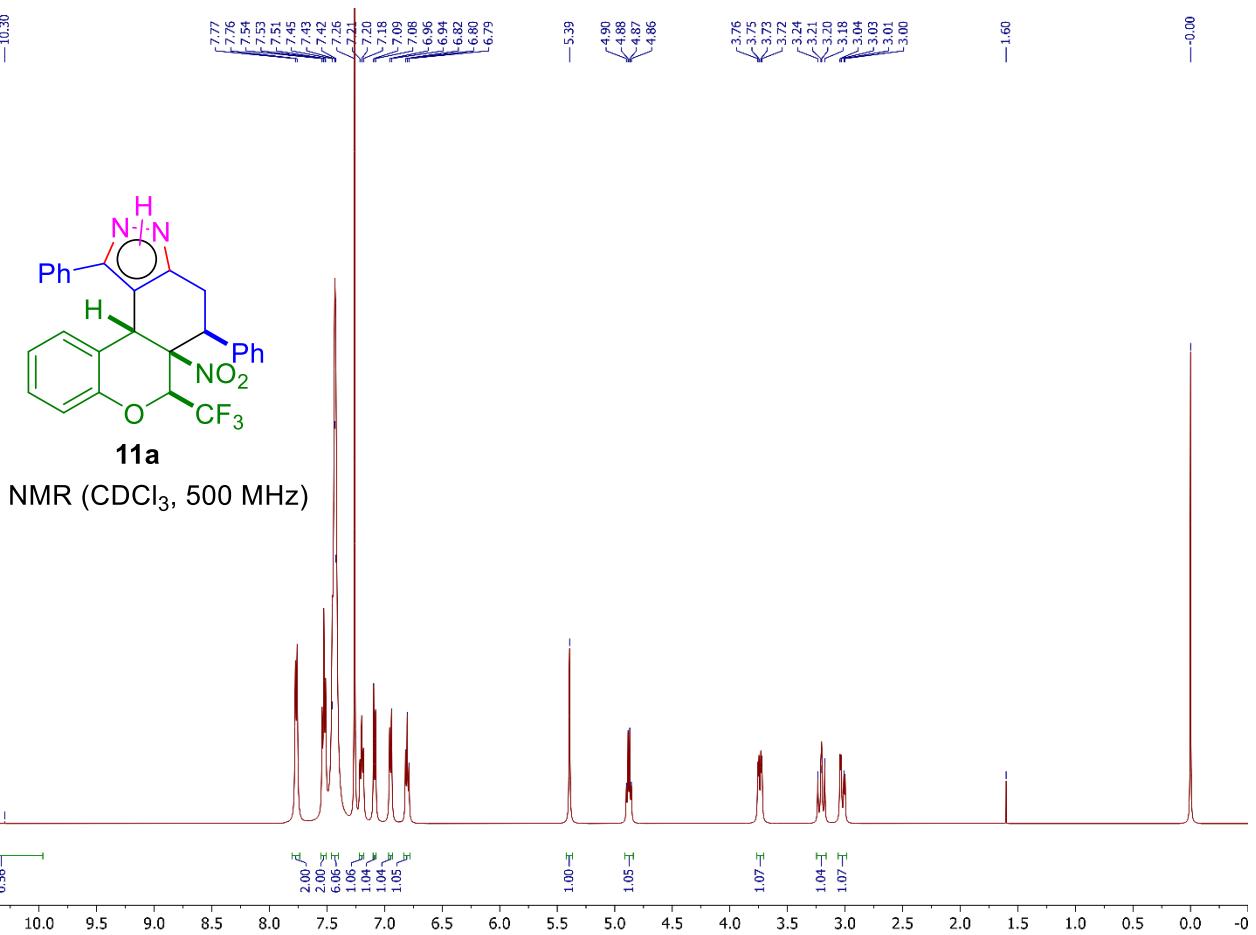


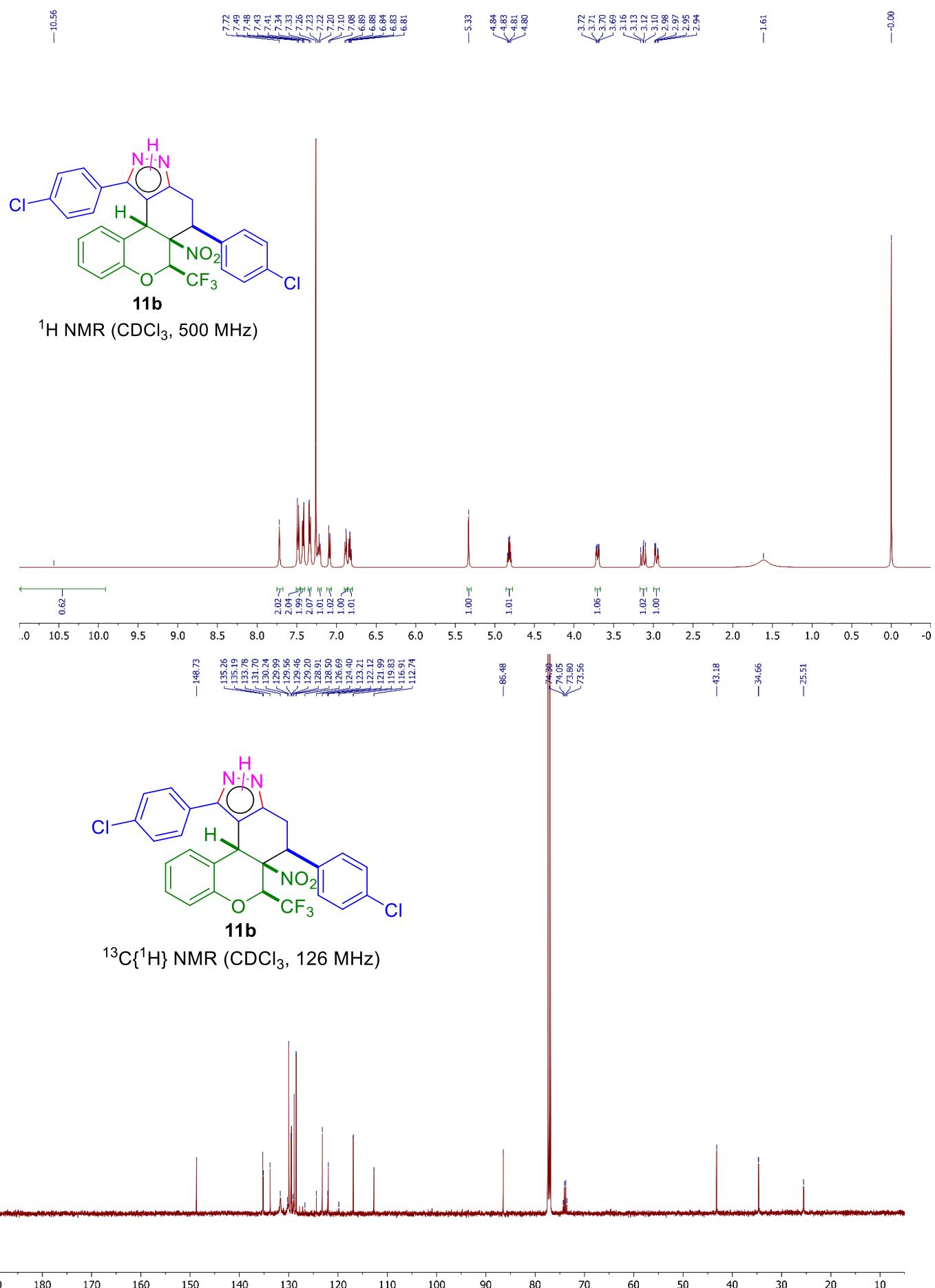


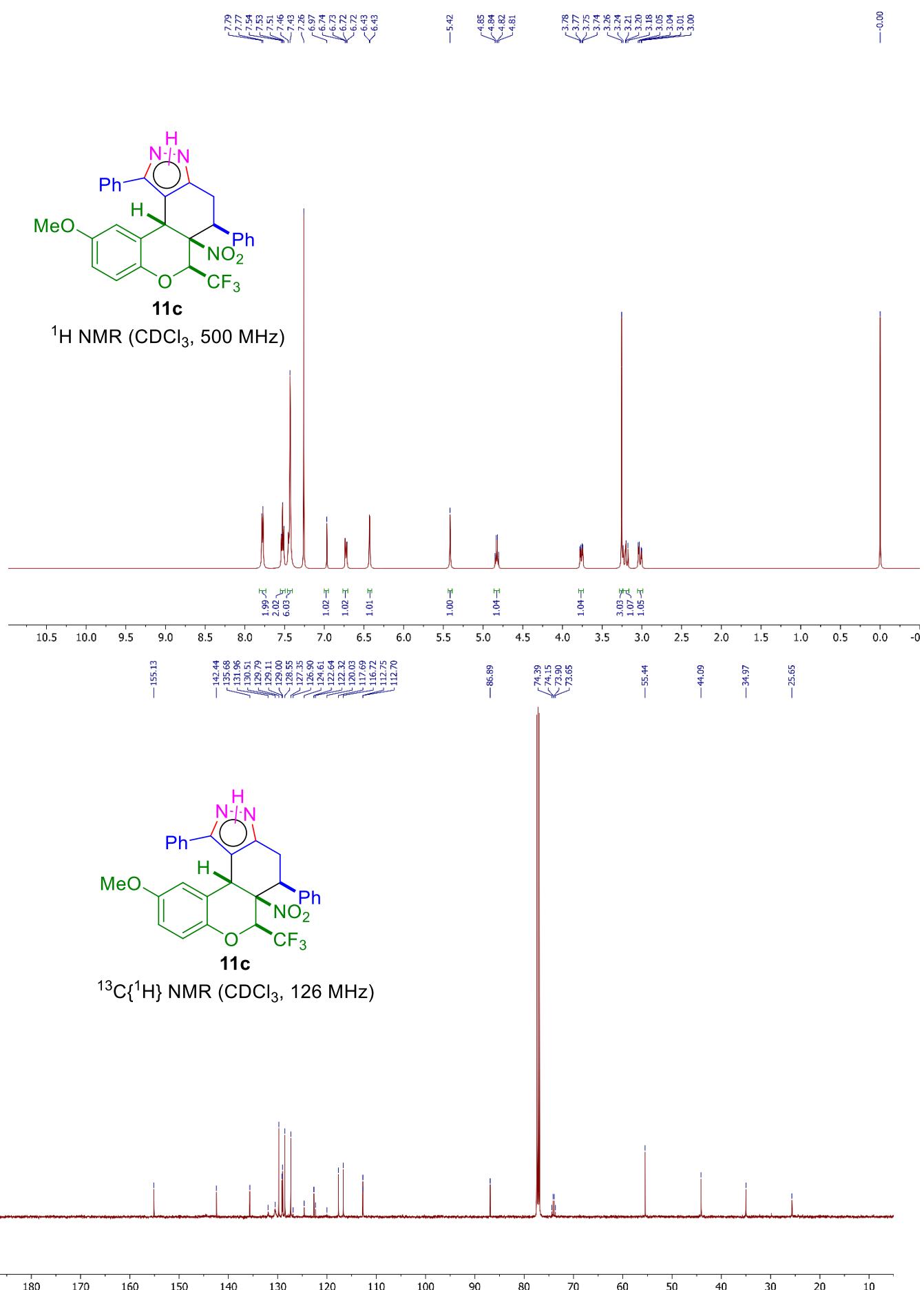
^1H NMR (CDCl_3 , 500 MHz)

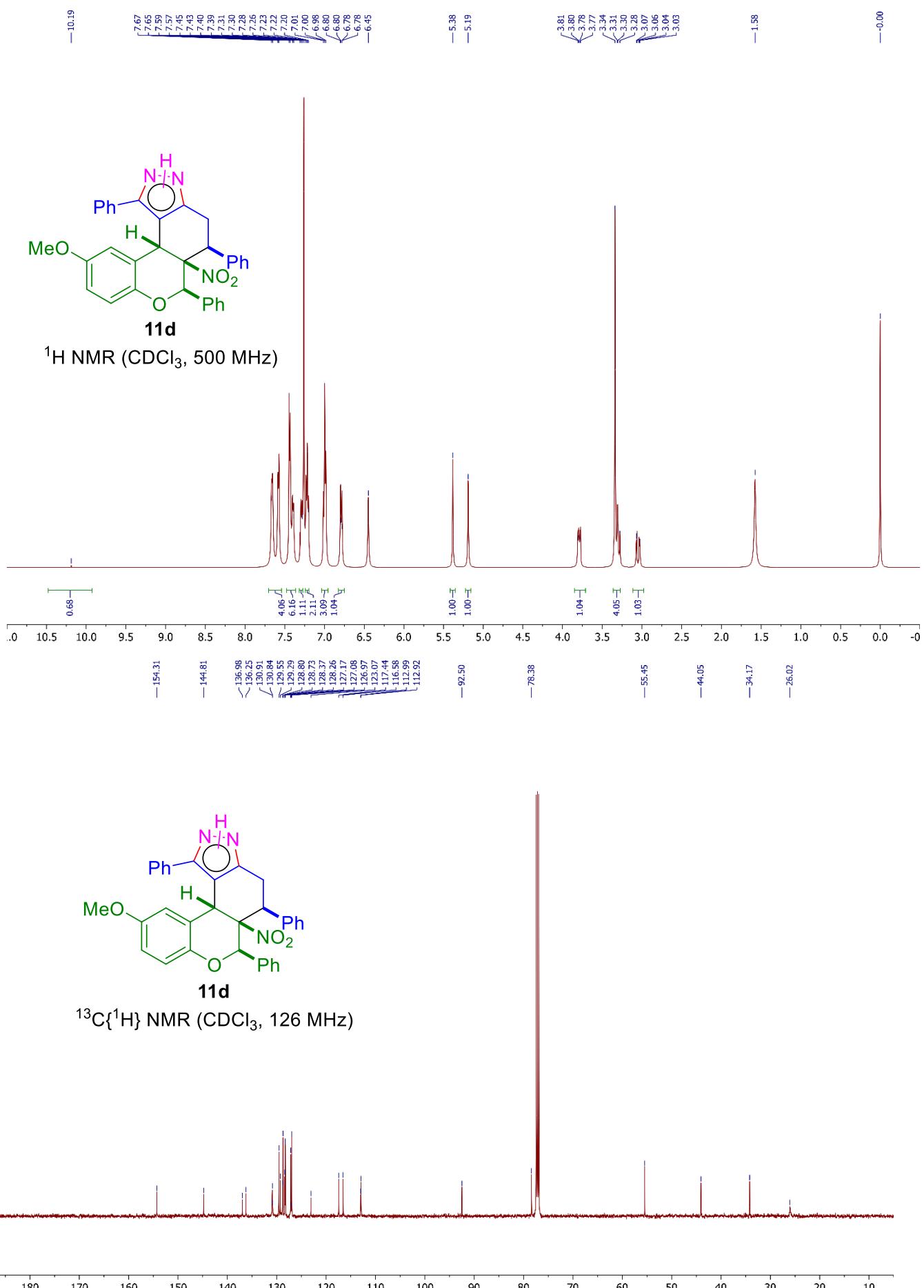


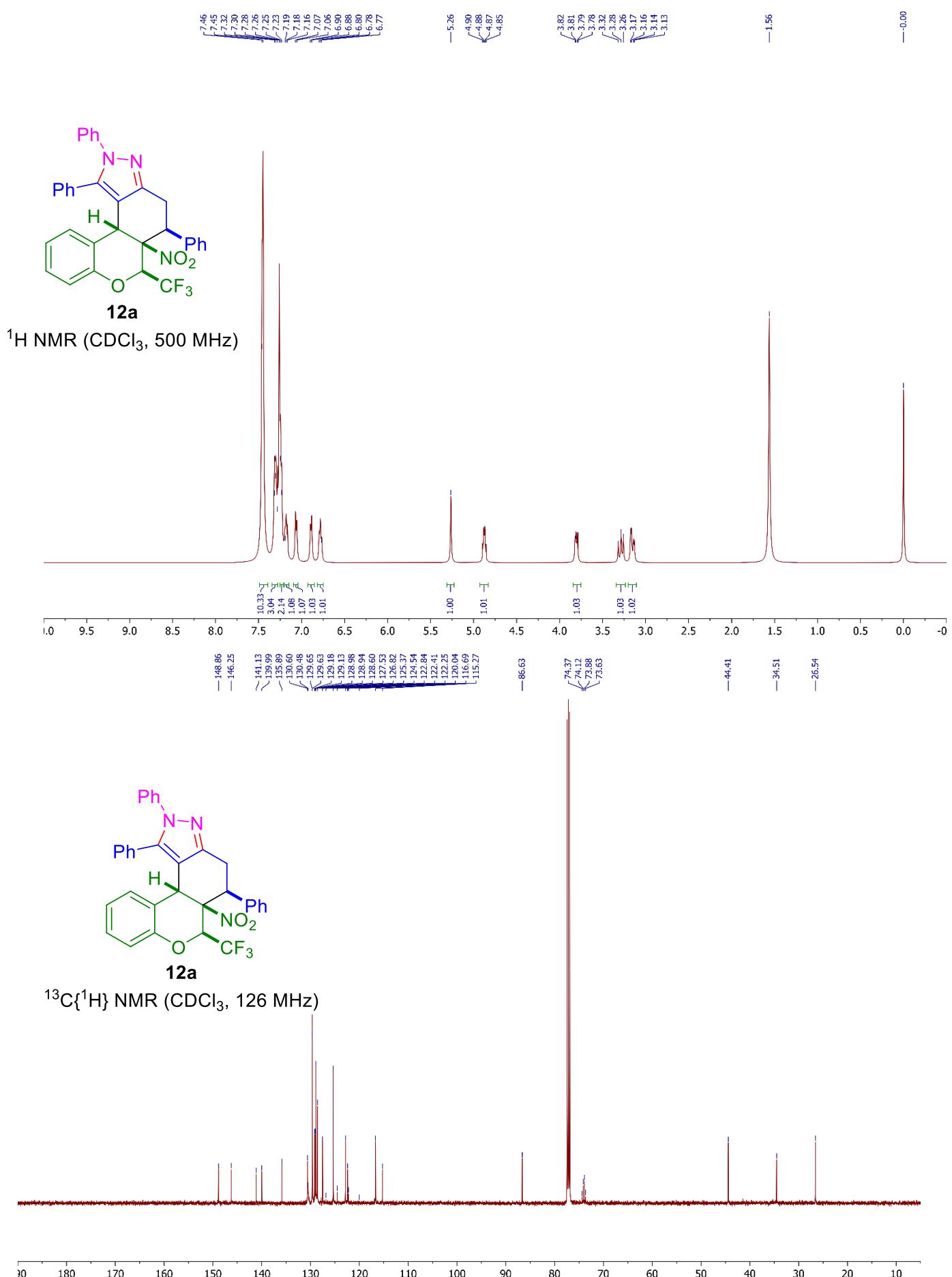


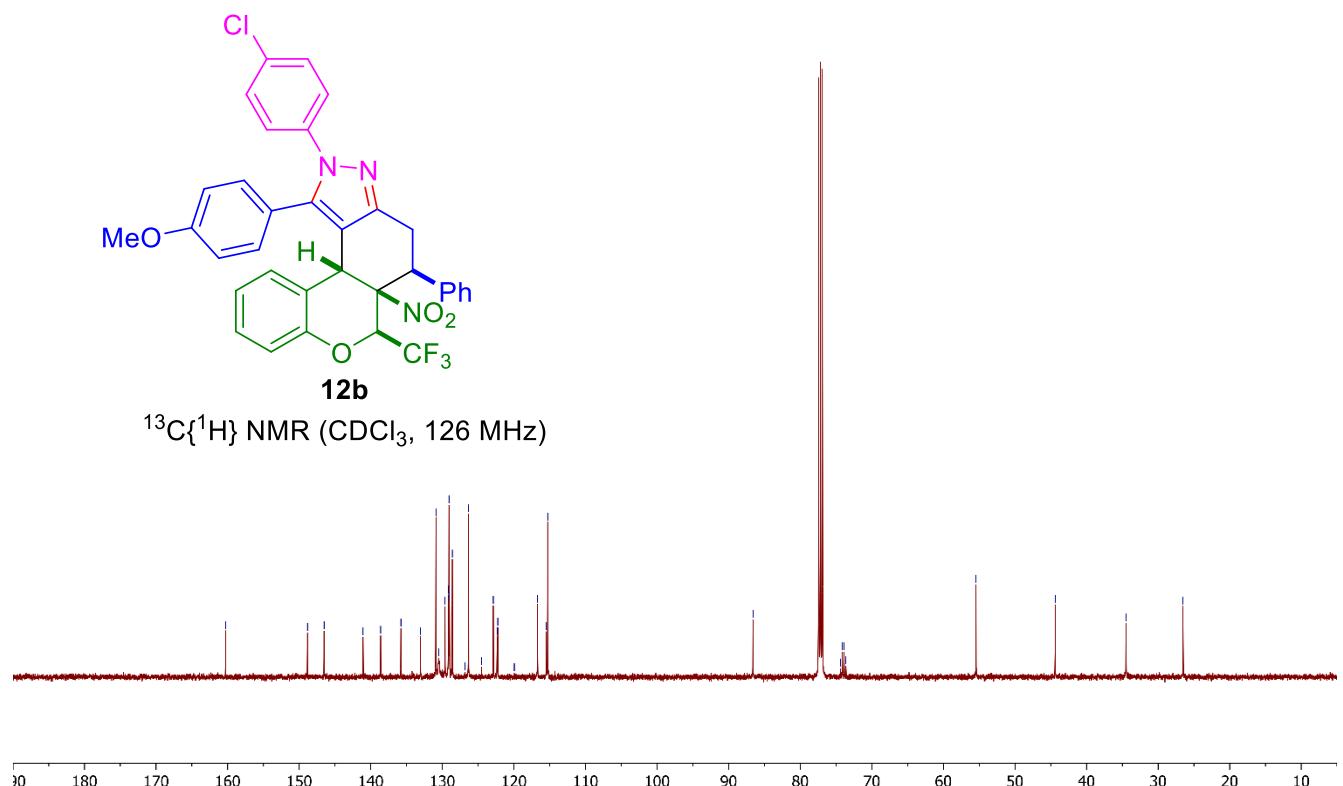
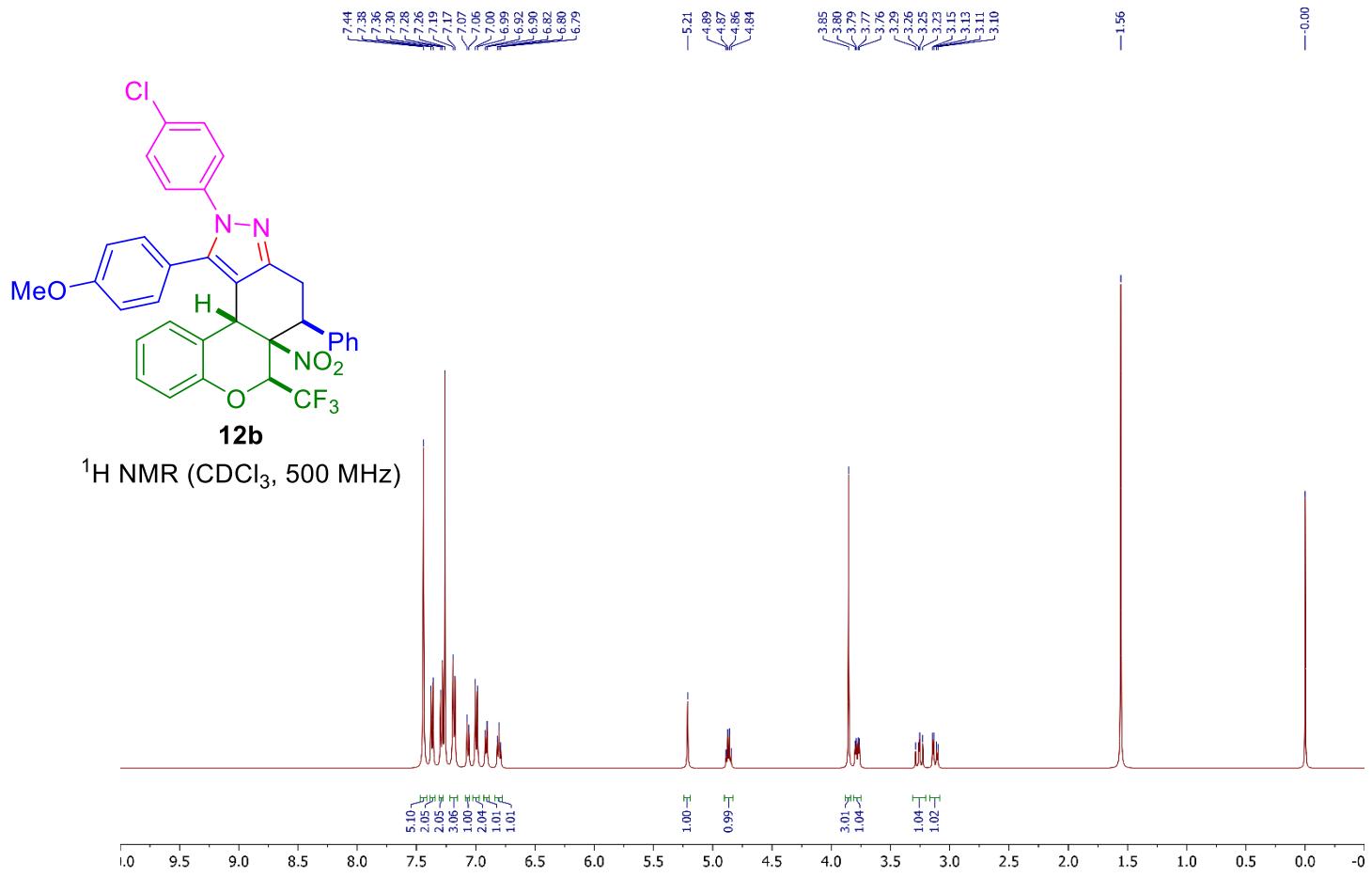


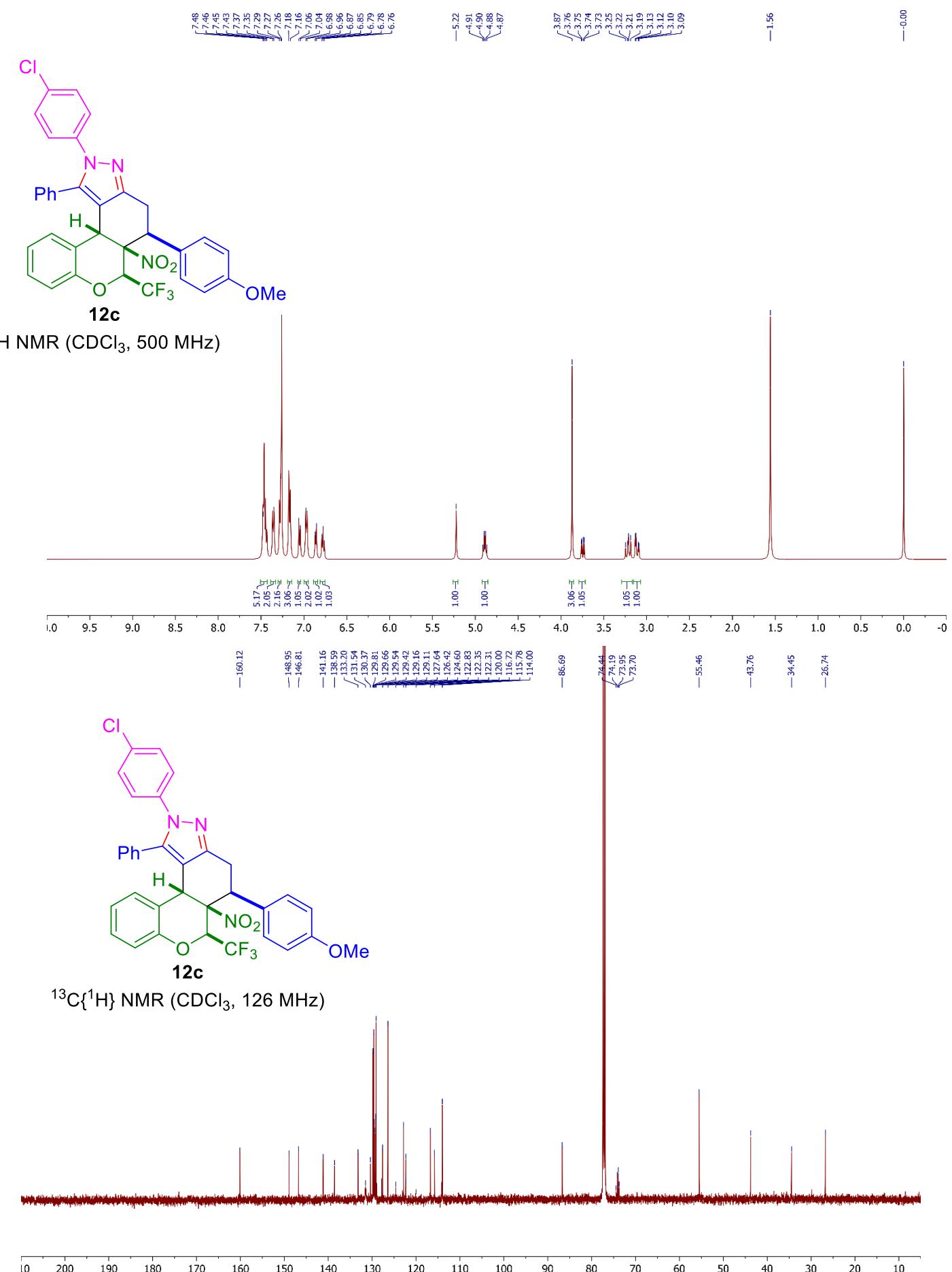


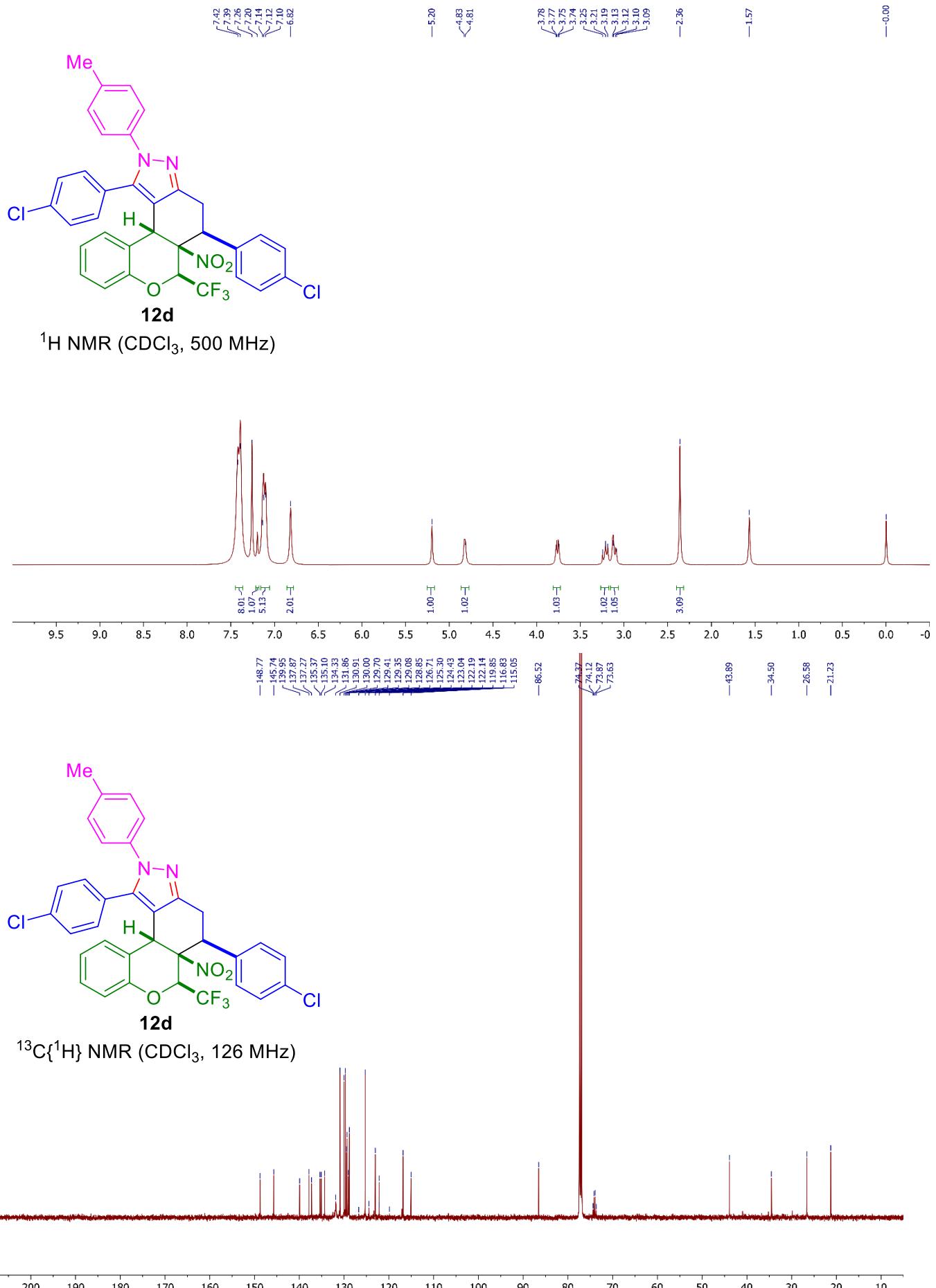


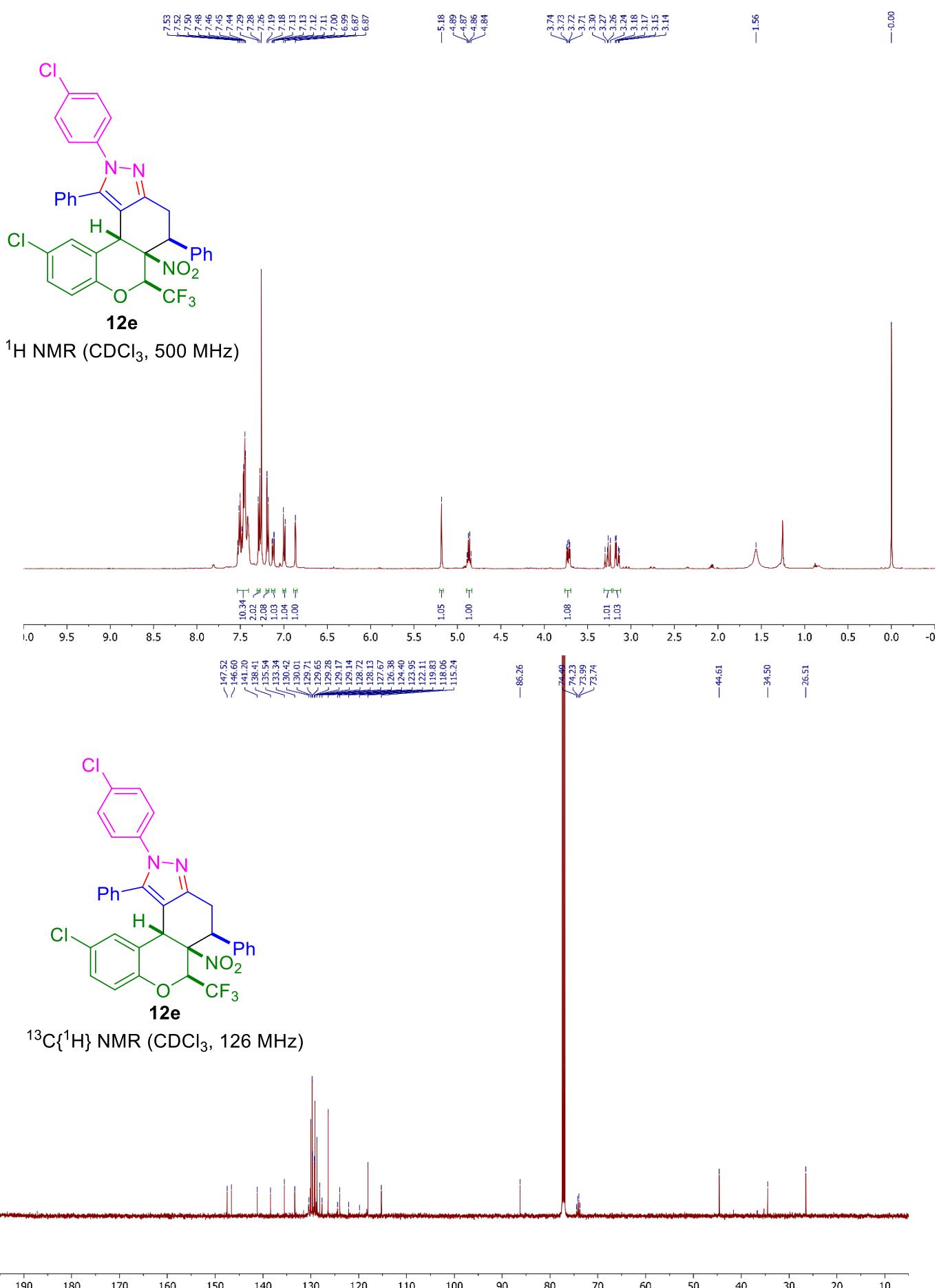


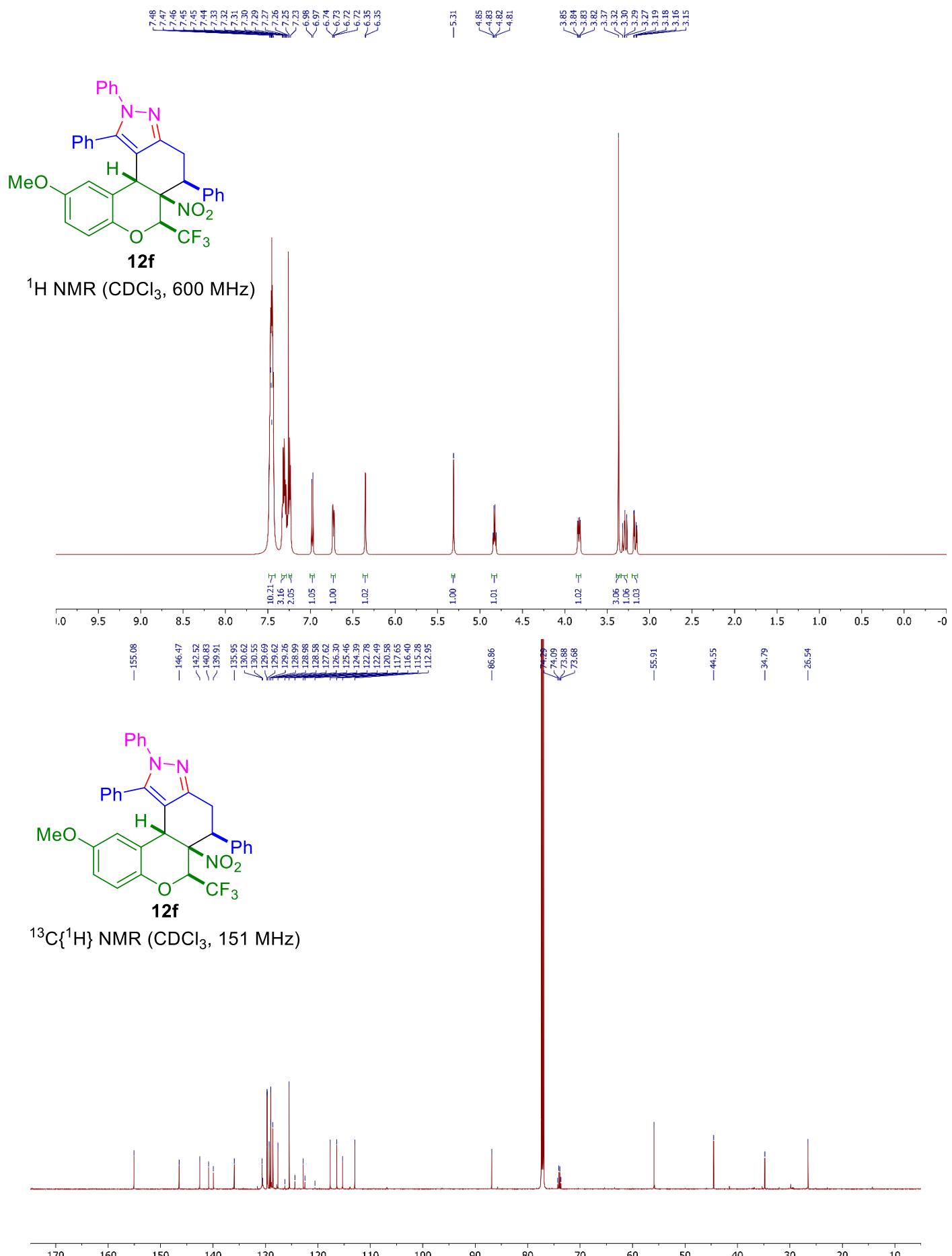


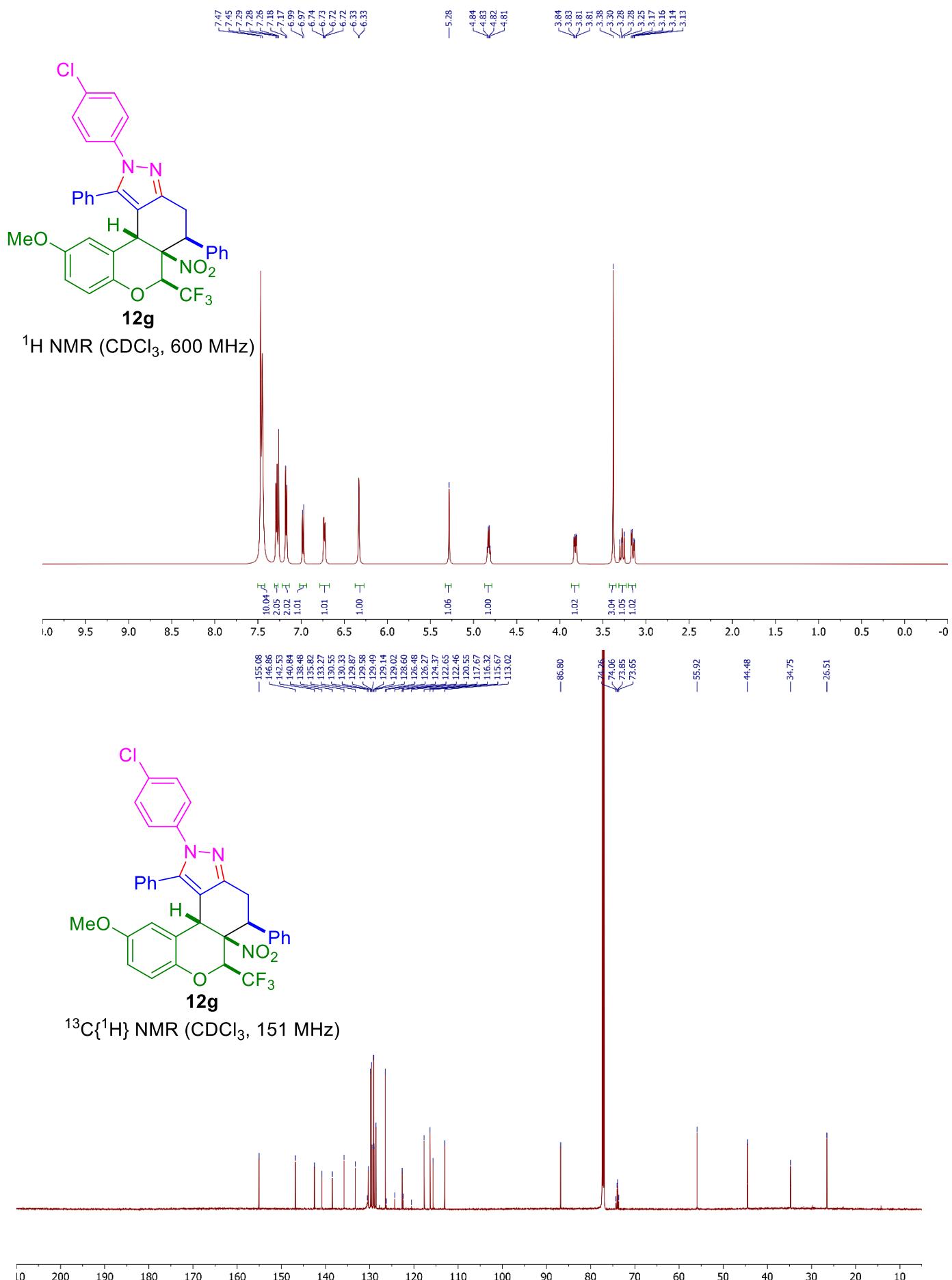


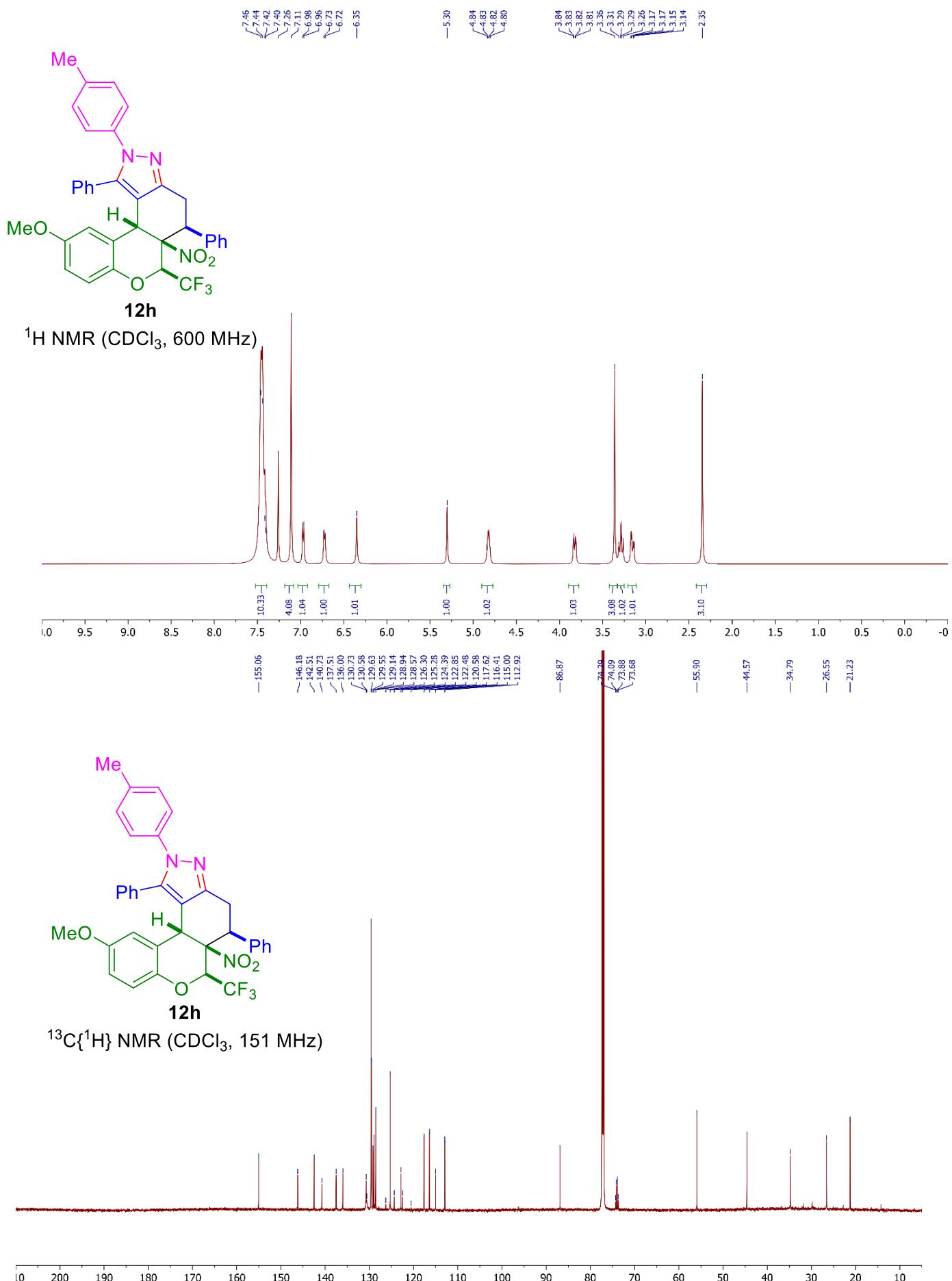


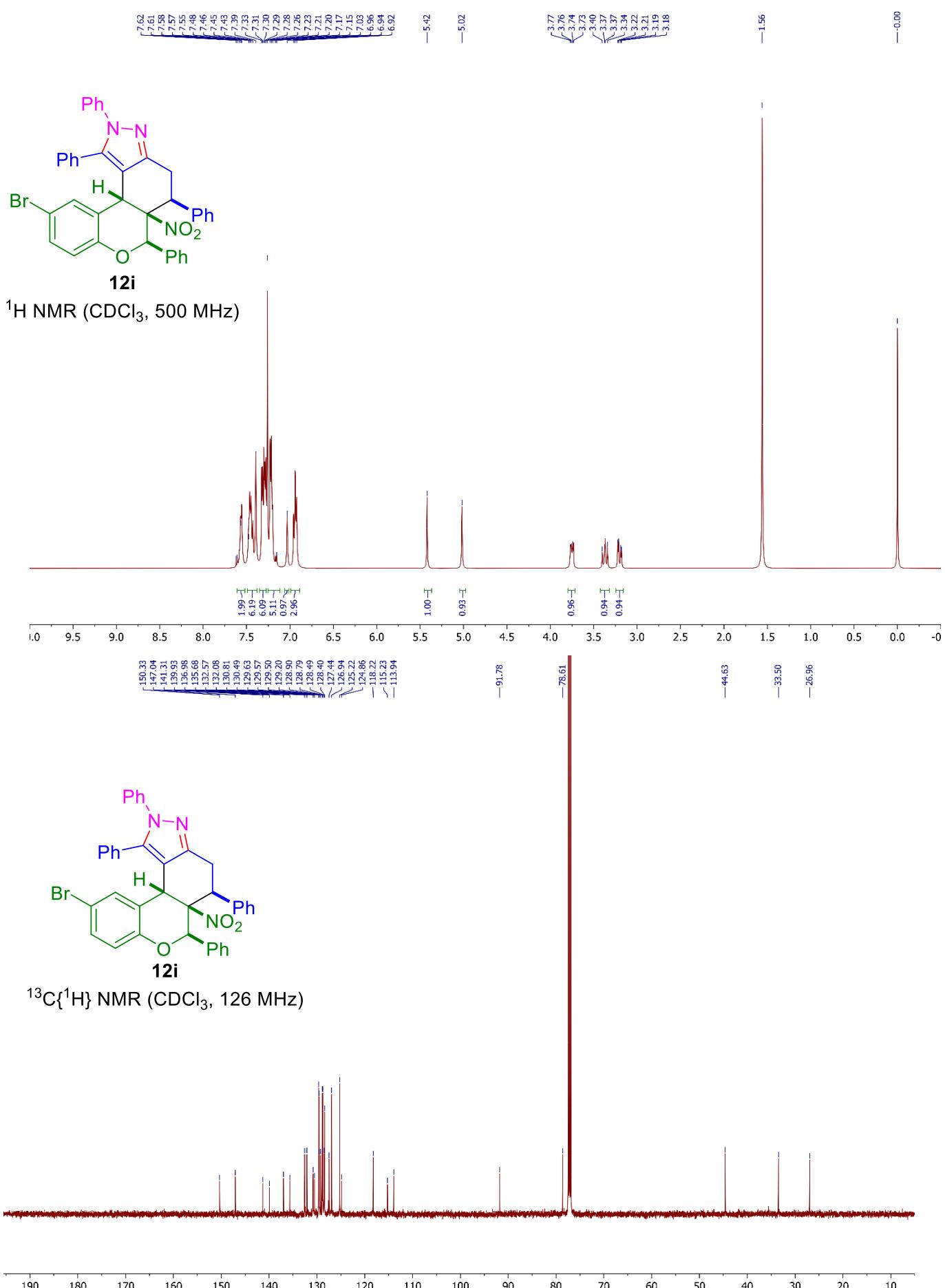


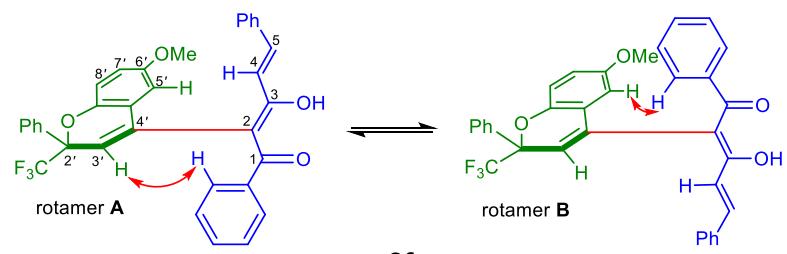




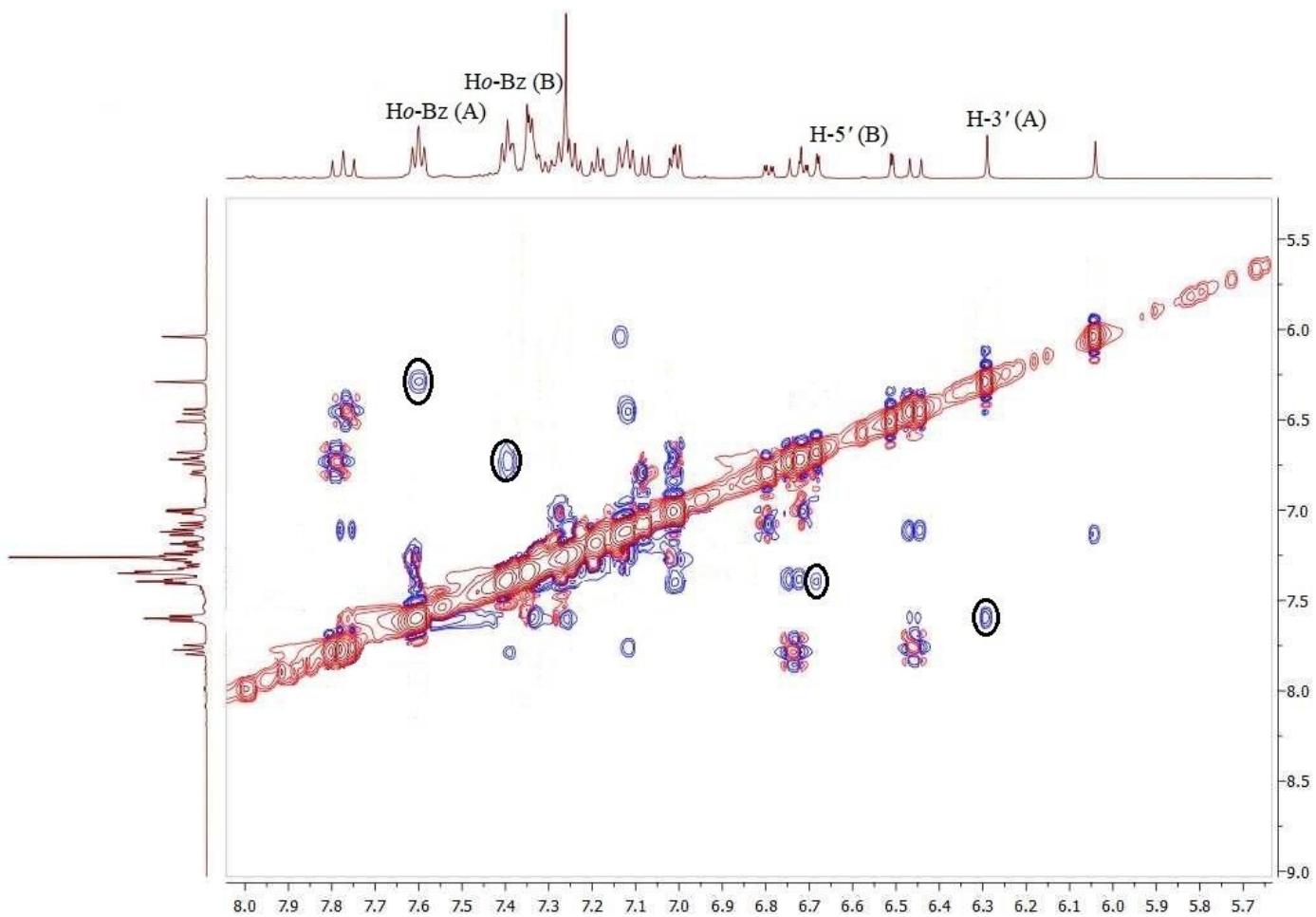


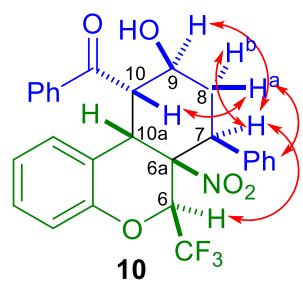






2D ^1H - ^1H NOESY NMR (CDCl_3 , 600 MHz)





2D ^1H - ^1H NOESY NMR (CDCl_3 , 600 MHz)

